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COPPER

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TO THE METAL

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COPPER MINE IN SPAIN
Showing open cut workings

(14' 50)

Frontispiece

PITMAN'S COMMON COMMODITIES
AND INDUSTRIES

C O P P E R

FROM THE ORE
TO THE METAL

BY
HUGH K. PICARD

ASSOC. ROYAL SCHOOL OF MINES
MEM. INST. OF MIN. AND MET.



SECOND EDITION

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PREFACE

TO THE SECOND EDITION

IN this second edition, the tables have been brought up to date so far as statistics are available. In certain particulars the descriptive matter has been amended to bring it more nearly in accord with present practice.

The author acknowledges with thanks assistance he has received from Henry Lavers, of Minerals Separation, Ltd., in regard to Flotation and from James Wilding, Metallurgist, for information as to recent American practice. His thanks are also due to the publishers of *Quin's Metal Handbook and Statistics* for permission to quote from their Tables.

LONDON, 1928

PREFACE

IN this volume the author has endeavoured to present in connected outline an account of the processes employed in the production of copper, from ore to metal. The subject is necessarily large and complex, each section having given rise to writings and discussions by many technical authorities. Thus, there already exists a considerable mass of literature bearing upon the technics of this branch of metallurgy. The author, therefore, does not address the advanced student, nor the practical metallurgist, but rather those who seek a general knowledge of the methods involved. It is hoped that the references given will be of use to those wishing for more detailed information on any particular point, as these indicate standard works by recognized authorities.

The metallurgy of copper has undergone important changes during recent years, which have resulted in material alterations in procedure from methods hitherto regarded as standard. These developments are due, mainly, to the evolution of the basic-lined converter, to the introduction of flotation concentration—with the consequent increased use of the reverberatory furnace in smelting—and, finally, to important advances in the hydrometallurgy of copper ores.

The author wishes to acknowledge valuable assistance from H. L. Sulman, F.I.C., M.I.M.M., in supplying suggestions and revising the proofs, and from F. H. Wintle, A.R.S.M., for several details of recent practice. His thanks are further extended to H. A. Latimer, late General Manager to Messrs. Williams, Foster &

Co., and Messrs. Pascoe, Grenfell & Sons, Ltd., Swansea, for information on the marketing of ores and metal in Great Britain, and, finally, to those who have kindly lent illustrations.

The works of several well-known authorities and technical Journals have been freely used, recognition of which, the author believes, has been given in each instance; but he wishes particularly to mention the assistance he has derived from—

- | | |
|------------|--|
| Peters | <i>Modern Copper Smelting.</i> |
| „ | <i>Principle of Copper Smelting.</i> |
| Hofman | <i>Metallurgy of Copper.</i> |
| Greenawalt | <i>Hydrometallurgy of Copper.</i> |
| | <i>Transactions of American Institute of Mining Engineers.</i> |
| | <i>Transactions of Institution of Mining and Metallurgy.</i> |
| | <i>Transactions of American Electro-Chemical Society.</i> |
| | <i>The Engineering and Mining Journal.</i> (N.Y.) |
| | <i>Metallurgical and Chemical Engineering.</i> (N.Y.) |
| | <i>The Mining Magazine.</i> (London.) |
| | <i>The Mining Journal.</i> (London.) |

HUGH K. PICARD.

LONDON, 1916.

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COPPER

CHAPTER I

COPPER : ITS PROPERTIES AND SOURCES OF SUPPLY

COPPER has been known since the earliest times, its employment in the alloyed form of bronze (doubtless smelted from impure copper and tin bearing minerals) having been common before the discovery of iron. The metal is said to derive its name from the Island of Cyprus (Gr. *κύπρος*) whence the Romans obtained their supplies of ore. Copper is distinguished from all other metals by its colour, a freshly-broken piece of pure metal showing a hackly fracture of rose-pink tint : it is highly malleable and ductile, and can be rolled into sheets or drawn into wires. Copper tubing or rolled sheet may be softened ("annealed") by heating to a cherry-red colour and allowing it to cool slowly or by quenching in water ; it conducts electricity freely, being second only to silver in this respect.

The atomic weight of copper is 63·43.¹ Its specific gravity varies according to the treatment it has received, rolled copper being denser than the cast metal ; the variation is between 8·80 and 8·95. It has a melting point of 1083°C.²

The uses of copper are so well known as to require but passing reference. Among the more important are : wire for electrical and other purposes ; sheets for ships' plating, boiler fire-boxes, and for a large variety

¹ Table, *Annuelles Internat. de Constants*, 1912.

² *Ibid.*, 1911.

of industries ; tubes, rods, domestic utensils, etc., and as an ingredient of many important alloys.

For industrial uses, copper is generally required in a state of fairly high purity ; this is especially the case for electrical work, as the conductivity of the element is impaired by the presence of other metals. For certain purposes, however, the presence of a small amount of arsenic is not disadvantageous, as it appears to correct the injurious effects of other more deleterious impurities, such as bismuth. To conform to the "British Specification for Copper Tubes"¹ suitable for screwing and capable of standing pressure, the copper must be 99·25% purity, and of the balance 0·25% to 0·45% must consist of arsenic.

Alloys.—Copper is the chief constituent of brass and of bronze, the former being essentially its alloy with zinc, and the latter with tin. It enters largely into the composition of many other important alloys, such as gunmetal, aluminium bronze, "Muntz-metal," "Delta-metal," etc. The terms "brass" and "bronze" have been used to express a number of alloys of varying composition, and an attempt has been made to standardize their employment by a "Committee on the Nomenclature of Alloys" appointed by the Institute of Metals.² Their report recommends that "the term 'brass' is to be used as an abbreviation of the words zinc-copper, . . . thus when the word brass alone is employed it shall denote an alloy of zinc and copper only, containing more copper than zinc. . . . The term 'bronze' is to be used as an abbreviation of the words 'tin-copper,' . . . it shall denote an alloy of tin and copper only, containing more copper than tin." The presence of a third metal in the alloy would be

¹ Engineering Standards Committee Report, No. 61.

² *Journal of the Inst. of Metals*. Vol. XI, p. 50.

ITS PROPERTIES AND SOURCES OF SUPPLY

denoted by prefixing such metal: thus, "tin-brass." Up to the present, however, these definitions have not been adopted by the trade, for reasons not difficult to appreciate.

The following abbreviated list of typical copper alloys is taken from Roberts-Austen¹—

	Copper ¹ %	Zinc %	Tin %	Other Constituents.	Uses and Remarks.
Brass . . .	63-72,	27-34	—	—	Typical brass
" . . .	70 29	29 26	0·17	Lead 0·28	Wire. Always brittle if Pb. reaches 2%. Tin may vary from ·1 to 0·5
Muntz-metal .	60-62	38-40	—	—	Ships' sheathing
Gunmetal . .	91·00	—	9·00	—	For ordnance
Bronze . . .	80-90	7·0	18-12	—	Bearings for heavy axles
Aluminium bronze	90·00	—	—	Aluminium 10·0	Tensile strength, 96,434 lb. per sq. in.
Phosphor bronze	82·20	—	12·95	Lead, 4·28 ; Phosphorus, 0·52	—
Manganese bronze	83·45	—	—	Manganese, 13·48 ; Iron, 1·24 ; Carbon, 0·11	Yellowish grey
Delta-metal .	55·10	43·47	—	Iron, 1·08 ; Lead, 0·37 ; Phosphorus, 0·10	—
² Fuse cap of German shell	55·4	42·5	—	Arsenic, 0·07	—
² Stock brass rod	64·7	35·2	—	—	—
² Brass water-tap	69·7	25·8	1·1	Lead, 3·4	—

Standard "yellow brass," according to Percy Longmuir,³ consists of copper 70%, and zinc 30%; while standard gunmetal carries copper 88%, zinc 2%, and tin 10%. Brass-rod, to be used for turning, should contain a little lead, as this prevents the metal from tearing under the action of the turning tool; in brass, a little arsenic is sometimes considered desirable.

¹ *Introduction to the Study of Metallurgy*; 4th Ed., p. 133.

² From analyses in the author's laboratory.

³ *The Foundry*, Oct., 1911, p. 74.

The *Brass World and Platers' Guide* for 1910 gives a list of alloys from the U.S.A. Government Specifications, from which the following are selected, the figures denoting percentages—

Commercial Brass. Copper 64–68; Zinc 32–34; Iron 2 (maximum); Lead 3 (maximum).

Gun-bronze. Copper 87–89; Tin 9–11; Zinc 1–3; Iron 0·06 (maximum); Lead 0·2 (maximum).

Muntz-metal. Copper 59–62; Zinc 39–41; Lead 0·6 (maximum).

Cast Naval-brass. Copper 59–63; Zinc 35·5–40·5; Tin 0·5–1·5; Iron 0·06 (maximum); Lead 0·6 (maximum).

Phosphor-bronze. Copper 80–90; Tin 6–8; Zinc 2–14; Phosphorus 0·3; Iron 0·06 (maximum); Lead 0·2 (maximum).

Sheet-brass and tubing. Copper 60–70; Zinc 30–40; Lead 0·5 (maximum).

Brass rods. Copper 62–63; Zinc 37–40; Lead 3 (maximum).

Copper in Coinage.—British bronze coinage is composed of copper 95%, tin 4%, zinc 1%. The “Standard silver” coin contains 7·5% and the “Standard gold” coin 8·33% of copper as the hardening alloy. When in 1920 the price of standard silver rose to over five shillings per ounce, the silver coinage was reduced in silver contents to 50%, the alloy metals being approximately 41% copper and 9% nickel. From 1922 to 1926 50% of copper only was employed as the base metal. The 1928 coinage still contains only 50% of silver with copper as the principal alloy. Nickel coins used in the British colonies and elsewhere contain copper 75%, nickel 25%. Alloys of copper and nickel are extensively employed in the arts. Among these may be mentioned nickel silver of very varying

ITS PROPERTIES AND SOURCES OF SUPPLY

composition, but usually containing about 50–60% of copper, 20% of nickel, and 20% of zinc; Monel metal (copper 28%, nickel 68%); Constantin, resistance metal (copper 60%, nickel 40%).

Brass-making.—In brass-making the copper is first melted, the zinc and other ingredients being then cautiously added. The surface of the metal is covered with charcoal to prevent oxidation and to assist in the reduction of the copper oxide, always present to a small extent in commercial copper; the beneficial effect of phosphorus in phosphor-bronze, and of aluminium and manganese, when employed, is also probably due in part to a similar deoxidizing action.

Copper Production.—On account of its many specific

WORLD'S PRODUCTION¹

	1923 ²	1924 ³	1925 ³	1926 ³
United States . . .	684,540	819,000	854,000	878,000
Mexico . . .	54,920	49,150	59,123	62,303
Canada . . .	36,496	51,008	56,239	64,124
Cuba . . .	10,853	12,742	13,128	13,034
Total North America .	786,809	931,900	982,490	1,017,461
Bolivia . . .	10,654	8,200	7,500	7,100
Chile . . .	203,256	209,855	209,654	223,015
Peru . . .	43,856	38,495	41,180	42,703
Total South America .	257,766	257,780	259,834	273,818
Austria . . .	1,540	4,465	3,665	4,099
Germany . . .	17,000	21,495	25,353	28,810
Norway . . .	8,000	10,913	12,125	13,779
Russia . . .	2,000	3,600	7,251	13,228
Spain and Portugal .	51,815	60,713	63,933	63,933
Sweden . . .	4,700	3,086	2,866	2,300
Jugoslavia . . .	6,837	8,987	8,048	10,692
Total Europe . . .	91,892	118,761	130,957	135,699
Asia . . .	64,790	70,756	77,013	77,377
Australasia . . .	17,946	15,711	13,800	11,244
Africa . . .	73,909	114,700	118,180	108,010
Other countries . . .	7,000	10,000	4,409	4,409
Grand Totals . . .	1,300,112	1,514,017	1,586,683	1,628,018

¹ From *Quin's Metal Handbook and Statistics*.

² Metric tons. ³ Tons of 2,000 lb.

applications copper is industrially one of the most important of the non-ferrous metals, its world-production being approximately equal to that of lead. The table on page 5 shows the world's production of copper for the years 1923-1926.

It will be seen that in the year 1926 the United States produced 53.9% of the total amount, and is thus the most important copper producer.

The production of copper from ores mined in the United Kingdom is relatively negligible though appreciable amounts of raw and partially smelted ores are imported for treatment. In recent years this has amounted to from 35,000 to 40,000 tons per annum.

The production of sheets, rods, tubes and copper sulphate for home use and export constitutes an important industry. Exports of copper sulphate mainly to vine-growing countries average about 40,000 tons per annum.

Copper Minerals.—Copper-bearing minerals are very widely distributed in practically all countries, though not always in payable quantity. In Great Britain—now so small a producer—they are met with chiefly in Cornwall, and to a lesser extent in Derbyshire, Cumberland, and certain parts of Scotland. Ireland also possesses copper mines which have been commercially worked in the recent past.

The copper minerals of chief commercial interest as forming the most important supplies, may be divided into two classes—the sulphide and the oxidized minerals.

SULPHIDE MINERALS

CHALCOPYRITE (or "copper pyrites")	($\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$)
CHALCOCITE (or "copper glance")	(Cu_2S)
ERUBESCITE (or "bornite")	($3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$)
TETRAHEDRITE ("grey copper" or "fahlerz")	(Cu_3S , with antimony and arsenic sulphides, etc.)

Of the sulphide minerals copper pyrites and chalcocite are the principal sources of the metal, though bornite is also a contributor. Tetrahedrite, besides being far less common, is objectionable from the smelters' point of view on account of the other metallic impurities it contains, particularly antimony and arsenic, though it frequently contains notable amounts of silver which render its treatment profitable.

OXIDIZED MINERALS

MALACHITE ("green carbonate of copper")	($\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2$)
CUPRITE ("red oxide of copper")	(Cu_2O)
TENORITE ("black oxide of copper")	(CuO)
AZURITE ("blue carbonate of copper")	($2\text{CuCO}_3 \cdot \text{CuH}_2\text{O}_2$)
CHRYSOCOLLA	($\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$)
ATACAMITE	($\text{CuCl} \cdot 3 \text{CuH}_2\text{O}_2$)
BROCHANITE	($\text{CuSO}_4 \cdot 3 \text{CuH}_2\text{O}_2$)

The first of these is, commercially, the most important, whilst the last has recently become a source of copper which promises to develop considerably; it will be referred to in a later chapter under "Wet Processes" for extraction. Deposits of "native" copper (i.e. copper in the metallic form disseminated through the rocky matrix), though comparatively rare, are found and worked on a very large scale in the Lake Superior district of the United States.

It will be noticed that the chief sulphide minerals contain their copper in the form of cuprous sulphide (Cu_2S). Cupric sulphide (CuS) is of less importance to the copper metallurgist, though on heating it is readily decomposed into cuprous sulphide and sulphur ($2 \text{CuS} = \text{Cu}_2\text{S} + \text{S}$).

From its special value as a source of copper, a brief consideration of the properties of cuprous sulphide is desirable, in order to understand the methods used for its treatment. As shown by its chemical formula, the

pure mineral consists of a combination of two atoms (or $2 \times 63.5^1 = 127$ parts by weight) of copper with one atom (32 parts by weight) of sulphur. It has a dark grey colour, and melts without decomposition at a lower temperature than metallic copper. On heating the substance in air the sulphur is oxidized to sulphurous acid (SO_2), the copper also combining with oxygen to form cupric oxide (CuO), known as the "black oxide" of copper. The above reaction represents the ultimate result of heating in air, but various intermediate changes take place. Thus, part of the sulphur oxidizes to sulphuric anhydride (SO_3), which, in turn, reacts on the cupric oxide simultaneously formed, yielding copper sulphate (CuSO_4). This compound is again broken up on further heating, losing the sulphuric anhydride (SO_3) which it had absorbed at a lower temperature, the final result being cupric oxide.

Cuprous sulphide, when protected from the action of the air, readily melts and combines with the sulphides of certain other metals which may be present, such as sulphide of iron (FeS), to form a "matte" or "regulus"—a fact utilized in the process of separating the metal from the barren rock with which it is associated. The heating of cuprous sulphide with cupric oxide results in the production of metallic copper, the sulphur of the sulphide and the oxygen of the oxide combining to yield sulphur dioxide (SO_2) with liberation of the metal: thus, $\text{Cu}_2\text{S} + 2\text{CuO} = 4\text{Cu} + \text{SO}_2$. Gibb & Philip have shown by numerous experiments that cuprous sulphide will not dissolve either sulphur or copper when heated with an excess of either element.²

¹ For practical purposes, the atomic weight of copper is taken at 63.5.

² *Trans. Amer. Inst. Min. Eng.* Vol. XXXVI, p. 667.

CHAPTER II

THE CONCENTRATION OF COPPER ORES

COPPER minerals occur in veins, in bedded deposits, and in irregular lenticular masses—the methods of mining being adapted to the nature of the deposit. It is not within the scope of this volume to deal with the various mining operations, our consideration being confined to the metallurgical processes applied to the ore after it has reached the surface.

In a majority of cases, the ore is not rich enough to be sent direct to the smelter for immediate conversion into metal; and, even in instances where such a course might be possible, it is frequently more advantageous to remove a proportion of the barren rock so as to avoid the expense of passing waste material through the smelting furnace. Under favourable circumstances, and if worked on a sufficiently large scale, ore containing as little as 1% of copper may be worked at a profit; but in such cases the small amounts of silver and gold which often accompany the copper in the ore, and are recovered therewith, are factors of commercial importance.

As the amount of waste material in the mined ore in general greatly exceeds the valuable portion, it is beneficial to reject a large amount of the former, if this can be done cheaply. This preliminary elimination of the waste is known as *concentration*.

It will be obvious that the principle of concentration is of great importance, and, if carried to its logical conclusion, would involve the rejection of all barren material in each of the successive steps of mining, crushing, and smelting.

In the succeeding paragraphs the process of concentration is briefly outlined, but it must be borne in

mind that local circumstances will always impose their own limiting conditions.

“Hand-picking” of the ore into richer and poorer portions is the simplest type of such a method. This selection is usually practised, in the first instance, in the mine itself, with the object of avoiding the despatch of any unnecessary barren rock to the surface.

A second more careful selection is commonly made when the ore reaches the mill. Here, the rough ore is examined by sorters, who divide it into a valuable portion, and waste. The ore is usually fed on to a travelling belt or table before which the sorters stand and make their selection as it passes before them, delivering the separated material either to suitable bins, or to conveyors for removal thereto. This work (in Europe frequently done by women, who develop considerable skill in detecting and separating the good lumps from the poor) simple as it appears, demands considerable judgment and quickness; since, when dealing with low grade ores, which carry small and irregularly occurring amounts of mineral, care must be exercised to prevent an undue proportion of good ore being rejected with the waste.

Picking, or selection, may be carried a stage farther by dividing the valuable portion into two grades, one being rich enough to be sent direct to the smelter, whilst the other is despatched to the mill for further concentration after crushing. Were the ore sufficiently rich to smelt direct, all crushing, except breakage of the largest lumps, would be avoided. This would result in a double advantage; crushing costs would be saved, and where the ore is to be smelted in a blast-furnace or cupola the avoidance of “fines,” or powdered material always produced by crushing, would be of material benefit.

Further selection of rich from poor ore can be made when the large lumps have been broken into smaller pieces. Obviously, with a non-uniform dissemination of valuable mineral through the matrix, some pieces so broken will be barren or poorer, whilst others will be richer, than the average of the unbroken piece. For example, if an ore-lump of 20 lb. weight containing 2% of copper be roughly broken so that the largest fragment weighs about 4 oz., probably several small pieces carrying, say 6% of copper, could be picked out, and a number of practically barren fragments rejected. Again, each of the 4 oz. pieces containing 6% might again be broken, from which a further selection could be made, and so on theoretically to the smallest particles. How far such operations of crushing and concentration can be carried in practice will depend on many circumstances, and no absolute rule can be laid down. As a general proposition, however, it may be said that where the mineral occurs massive in the rock, less step-by-step crushing and concentration will be necessary, but where the mineral is more finely and uniformly distributed through the matrix it is advisable to crush all the ore to fine powder before separating the valuable particles therefrom. The latter course involves a variation in the subsequent concentration treatment, which will be described later. Where the older method persists, the practice consists in the first instance in breaking the ore into coarse fragments, say, such as will pass through a ring $1\frac{1}{4}$ in. diameter. The coarser portion, or oversize, is separated from the undersize by screening or "trommelling," and the former concentrated by "wet" or gravity methods.

Jigging.—This consists in mixing the crushed ore with water, and passing the product, or "pulp," through specially devised machines. The heavier

mineral particles fall or settle by virtue of their higher specific gravity, while the lighter portions, which consist mainly of the barren rock, are carried forward and removed in the water current.

The water-concentration machine usually employed to separate the *larger* fragments of the copper mineral from the "gangue," or rock, is known as the "jig." In one form of this, the ore travels through a series of compartments fitted with sieve diaphragms, each of which carries a layer of heavy granular material forming the "bed." Water is caused to pulsate rapidly through the sieves, the conditions of flow, pulsation, etc., being so regulated that the heavier valuable portion of the mineral to be separated can settle upon the sieve-bed, whilst the lighter rock and the finer particles of any material not capable of settling against the vertical water pulsations pass over the bed and out of the machine. In one type the heavier particles work their way through the coarser ones which constitute the bed, collecting in the compartment beneath, whence they are periodically removed. In another form, the heavy mineral tends to accumulate *upon* the bed, and is continuously discharged through a horizontal slot provided for the purpose in the front of the apparatus.

The simplest form of jig is an oblong box with a V-shaped bottom, divided longitudinally by a vertical partition which does not reach the bottom (see illustration). On one side of the partition and at a convenient depth from the top is fixed the screen or sieve, of such mesh that the particles it is desired to concentrate can just pass through. Upon this rests the bed of heavy material (such as coarser mineral concentrate) of larger size than the mesh of the sieve. On the other side of the partition is a movable plunger, actuated by a variable

eccentric and connecting rod, which imparts a pulsating motion to the water filling the box proportionate to the number of revolutions and the throw of the eccentric.

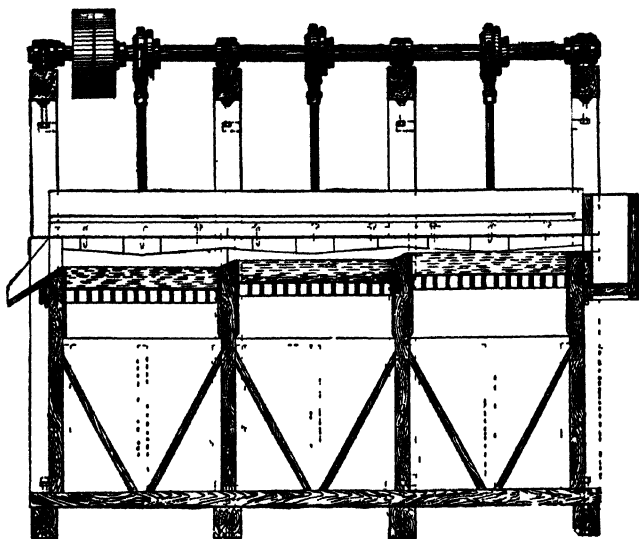
The machine is continuous in action, and receives at the feed end ore particles of suitable size carried by a stream of water. The heavier particles either work through the bed and accumulate in the V-shaped bottom, or may be removed through the slot discharge above the bed; the lighter gangue particles travel onwards and are continuously washed out over the end of the box.

From the simple form of jig described many developments and improved designs have been evolved, descriptions of which will be found in modern works on ore-dressing. The jig is a machine of high capacity, and once correctly adjusted, will work with the minimum amount of attention if regularly supplied with ore-pulp of the proper grade.

The jig concentrates are generally of sufficient richness to be sent to the smelting furnace, whilst the lighter or rejected portion may be poor enough to be run to waste; more often, however, it is necessary to crush the latter yet finer, and to separate the further mineral so liberated in other jigs adjusted to handle finer grade material. The finer portions which result from the first crushing are similarly graded into coarser and finer products, and these are treated in like manner.

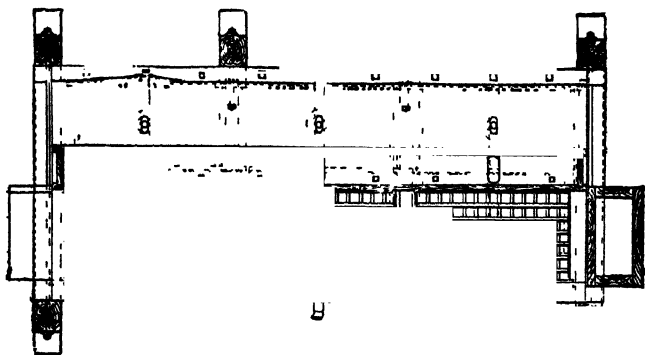
Jig treatment has thus a comparatively wide range of utility, and will deal with crushed material varying in size between $1\frac{1}{4}$ in. diameter and 0.04 in. (1 millimetre).

The size of particles below 0.05 in. in diameter is generally defined by the mesh of the sieve through which they will pass. In the standard sieve adopted by the Institution of Mining and Metallurgy the diameter of the wires forming the warp and weft is



Fraser & Chalmers, Ltd., Erith, Eng.

THREE-COMPARTMENT HARTZ JIG
(Sectional front elevation)



Fraser & Chalmers, Ltd., Erith, Eng.

THREE-COMPARTMENT HARTZ JIG
(Plan)

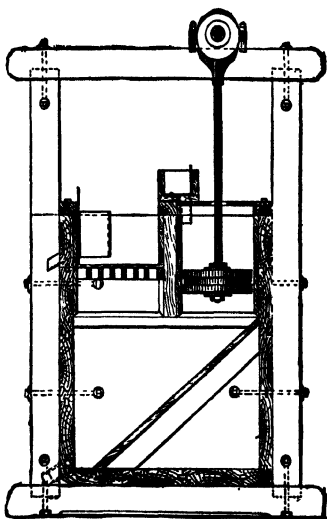
equal to the spaces between them, and the mesh-number which defines a given sieve indicates the number of apertures in one linear inch, measured parallel to warp or weft. Thus a "50 mesh" screen has fifty apertures per linear in., and as there are as many equal wire thicknesses and spaces in the length, the size of each aperture (or the diameter of a particle which will just pass through it) must necessarily be one-hundredth of an inch.

The lower limit in the size of particle suitable for efficient separation by jigs is about 12 mesh (i.e. a particle of one-twenty-fourth (0.0416) inch diameter).

But in the various step-by-step crushing operations a large proportion of still smaller particles, both mineral and gangue, is necessarily produced

These particles may be of "sand" size, say from about 15 to 120 mesh, or "fine sands" (120 to 200 mesh), whilst those below this limit—of which there will always be a considerable amount—are usually denoted as "slime" products, from their finely divided character and the slowness of their settlement in water.

With increasing fineness of diameter or grade the actual liberation of mineral from rock will naturally



Fraser & Chalmers, Ltd., Erith, Eng.

THREE-COMPARTMENT
HARTZ JIG
(Section)

approach more nearly to completeness, and, theoretically, dissociation should reach its ultimate limit if all the ore be ground to the condition of slime. In practice, however, the aim of the mill-man is to limit the production of slime to a minimum, for, though some will invariably be made, the separation and recovery of the finely ground mineral from equally finely ground gangue is a difficult operation, and at best very imperfect. Moreover owing to the friable nature of most copper minerals (which tend to break into fine particles more readily than the rock matter) the slimed portion of the ore is usually richer in copper, so much so that a large proportion of the metal in the slime may generally be accounted as loss. Hence, in practice, to slime a copper ore is usually tantamount to wasting it, so far as recovery by ordinary methods of water-concentration are concerned.

The practical aim of the crushing process being to secure the sharpest division of copper mineral from gangue in the *coarser* grade products and sands, the jig is employed to effect the saving of the mineral from the former, whilst the concentration of the copper from the sand too fine for jig treatment is relegated to further machines; these are usually "tables," of varying construction and design, though all more or less conform to the same broad principles of operation.

Concentrating Tables.—A type commonly used consists of a rectangular surface or "deck" of wood, some 15 ft. in length by 5 ft. in width, set at a slight inclination to its short axis and mounted on a frame to which can be imparted a rapid small reciprocating "throw" in the direction of its length. The wooden surface is usually covered with linoleum, or similar material, securely attached thereto; "riffles," or narrow strips of thin wood, each somewhat longer than the one

above it, are tacked lengthwise to the cover, the shortest near the top corner of the deck in the region of the pulp-feed, the longest close to the lower edge. Their ends thus form a diagonal across the table. The riffles present a series of slight hindrances to the flow of the sand-pulps which would otherwise travel uniformly from the feed area at the top corner to the discharge edge, according to the degree of the inclination given to the deck. Owing to the higher specific gravity of the mineral particles, to the slight frictional retardation of the surface to particles resting upon it, and to the mechanical hindrance of the successive riffles, the heavier minerals tend to accumulate in the spaces behind the latter; while the lighter rock sands, being less hindered, flow over the riffle obstructions in a more or less diagonal path, determined by the slope of the deck and by the number and nature of the reciprocations. The depleted sands are removed in a launder at the lower edge of the table, whilst the mineral values constantly move forward by the "throw," behind the hindering riffles towards the remote end of the table, where they are collected in a separate trough or launder.

Among the many efficient tables which have been developed for sand-treatment, the most widely used type is that known as the "Wilfley," to whose designers the credit for the origination of the riffle system is due.

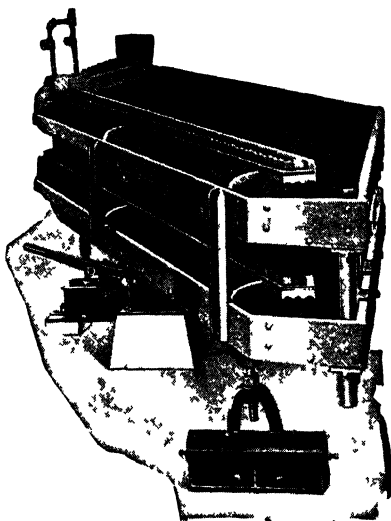
Another form of table illustrated is the "Deister," which is also extensively employed in America and elsewhere for the concentration of "sands," whilst a modified design finds useful application in the treatment of the finer or "slimes" portion of the ore. The drawing shows a "double-deck" table having twice the capacity of the single-deck form, whilst only occupying half the floor-space; duplication of the motion parts is also saved.

WILFLEY CONCENTRATING TABLE



Several other types of concentrating tables are constructed with one, two, or more decks, with the same object in view.

But upon the table the separation is not perfect, three products usually resulting : (1) "concentrate"—

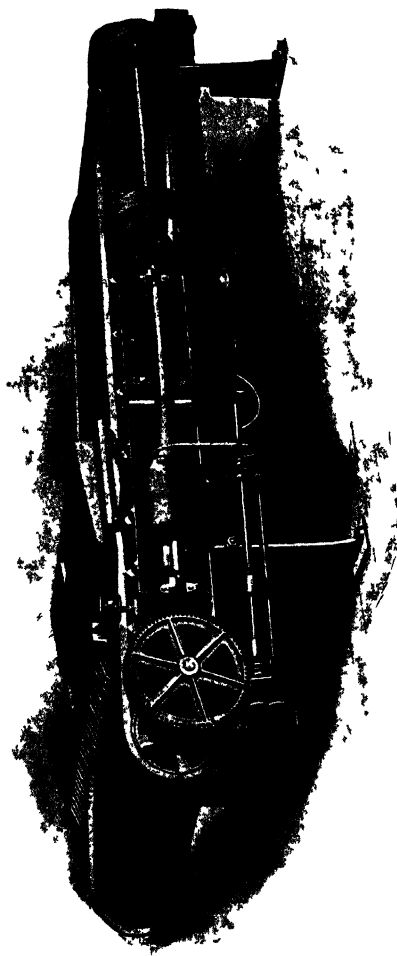


DEISTER CONCENTRATING TABLE

or that part richest in copper values, ready for the smelter ; (2) "middling"—a mixed product which is again treated upon a second table, often after having received another light crushing ; and (3) "tailing"—or sands sufficiently freed from mineral to be sent to waste.

Treatment of Slime.—Notwithstanding all precautions in crushing, some "slime" will inevitably be produced, and as this will necessarily be rich in copper a final concentration of some of the very finely divided mineral is usually attempted. Many forms of apparatus

have been designed for the purpose, one variety extensively employed being of "table" type, but specialized to the more exacting conditions involved, under the title of "slimer." Or the concentration of the copper from the slime pulps may be effected by causing them to flow down, or diagonally across, a rubber belt travelling slowly against the direction of the flow: the belt may also be given a small "side-shake," or transverse reciprocal motion. Machines of this form are called "vanners," of which the best known example is the "Frue Vanner." This consists of a broad endless rubber belt with raised moulded edges to prevent the pulp from being thrown over the sides, mounted on four rollers, the upper pair of which carry the continuously travelling working-surface: the lower pair guide the belt into and out of a tank, where the concentrates which cling to the surface are washed off by immersion in water. This system of belt and rollers is mounted on a frame, to which the side-shake is given by means of a crank and connecting rod. The belt travels continuously over the rollers at a gentle upward inclination and in a contrary direction to the flow of the pulp, which is fed upon the belt near its upper end by means of a suitable distributor. When the pulp meets the belt surface the secondary side-shake motion causes the heavier but fine mineral particles to sink and adhere to the rubber working face, whilst the lighter gangue remaining suspended more completely in the water, flows down and is discharged over the lower end. The upward travel of the belt carries the adhering concentrate over the head roller; the belt in returning face downwards dips into a tank of water placed under the vanner, in which the mineral is washed off and removed. The cleaned belt in due course returns over the lower rollers, again becoming the upper or working surface.



Fraser & Chalmers, Ltd., Erith, Eng.

THE FRUE VANNER

The terms "slimer" and "vanner" are somewhat loosely applied to a wide variety of appliances based upon "hindered flow" and "frictional resistance" factors, such as "buddles," revolving and stationary circular tables, etc. These, however, are not so extensively used as formerly for the recovery of copper, and space will not permit of their description.

The foregoing paragraphs convey but the bare outline of the operations and principles involved in concentration; the problems to be solved cover a great amount of theoretical and practical detail, scarcely less voluminous indeed than the subsequent metallurgy of the minerals so recovered. For more specific information upon these preliminary but important steps in the proximate recovery of copper minerals the student should consult one of the many textbooks on ore-dressing.

It will be understood that none of the methods or machines above dealt with are capable of affording complete separation. To divide the ore into nothing but clean concentrate on the one hand and barren gangue on the other is impossible by such mechanical means, and, even if possible, would generally be inadvisable on the score of the heavy cost of unlimited re-treatment operations. It must be remembered that the metallurgist's first, and indeed only, object is to obtain a maximum *profit* from his ore. He will not infrequently find a 70% net recovery of metal to yield a higher return in dividends than if he were to push his recovery to 80%; nevertheless he will constantly aim to improve his practice provided that the increased cost will be more than met by the gain in values obtained.

Flotation. In the preceding pages consideration has been given to the concentration of copper ores by methods depending on gravity. In recent years, however, concentration by "flotation" has been so

generally adopted that gravity methods have become almost obsolete in the treatment of sulphide ores.

Flotation is applicable not only to most sulphide ores but to many oxidized ores and such as contain their values in a metallic state.

Successful concentration by gravity methods is possible only in the case of an ore in which the mineral to be recovered is in a fairly coarse state of crystallization and of specific gravity substantially greater than that of the gangue or waste rock. Further, the ore must be crushed in such manner as to avoid so far as possible production of excessively fine or slimed mineral, since this in large measure is lost during the subsequent concentration operation. Careful classification or sizing is also necessary to secure the best results.

On the other hand, concentration by flotation is practically independent of classification, and provided the ore be crushed sufficiently finely to liberate the mineral from the rock, good results can be obtained even though the whole of the mineral be in a slimed condition. Many sulphide minerals and those of copper in particular are softer than the rock in which they occur, and consequently a relatively large proportion of the values are found in the slimes portion of the crushed ore, and on this account flotation possesses a great advantage over other methods of concentration.

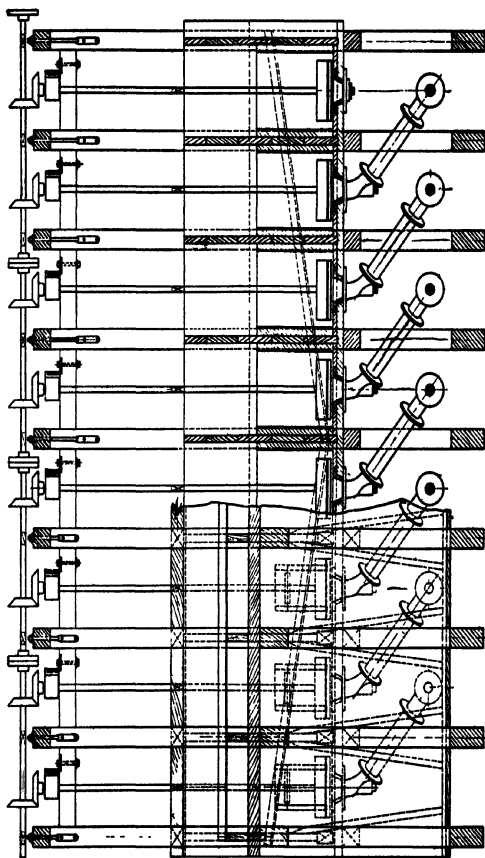
In its simplest form the flotation of metallic or sulphide particles may be observed on exposing a small portion of the crushed ore, previously moistened, alternately to air and water upon a smooth plate; if a little water be placed thereon and the plate be slowly and slightly tilted backwards and forwards, the oncoming edge of the water-film will be found to select and float many of the sulphide particles whilst those of the gangue remain submerged. The separation will be pronounced

if the water is very slightly acidulated ; still more so if the surface of the mineral be contaminated with the minutest trace of oil or grease.

The principles underlying the flotation of minerals have been widely discussed in various textbooks, and it will serve here to refer to them in the briefest manner. The treatment may be said to be based on the utilization of the surface tension forces that develop at the interfacial surfaces of the gas-liquid-solid contacts which result when a finely-crushed ore is suitably suspended in water in the presence of air or air bubbles. The surface-tension forces may be modified by absorption factors, and can therefore be intensified by reagents added for this purpose to the pulp during treatment.

The working conditions ensure a marked selectivity as between the sulphide minerals and the gangue by reason of the affinity of the sulphides for air and of the gangue for water. The air bubbles with their burden of sulphide particles collect to form a froth which floats at the water surface whilst the gangue remains wetted and sunken.

An early method of flotation may be exemplified by the floating of a slightly greased needle on water. The sulphide particles, especially if contaminated with oil, will float in this manner forming a continuous layer over a considerable surface of water. This process, known as "Film Flotation," has been used on a practical scale by De Bavay and others, but owing to the relatively large surface required for the flotation of a limited amount of mineral the method fell into disuse. Among early processes of flotation that of Potter was used extensively at Broken Hill for the treatment of zinc-bearing tailings from the gravity concentrators. In 1906 what is known as the "Froth Flotation" process was put into successful operation at Broken Hill, since when its use has so greatly extended that at the



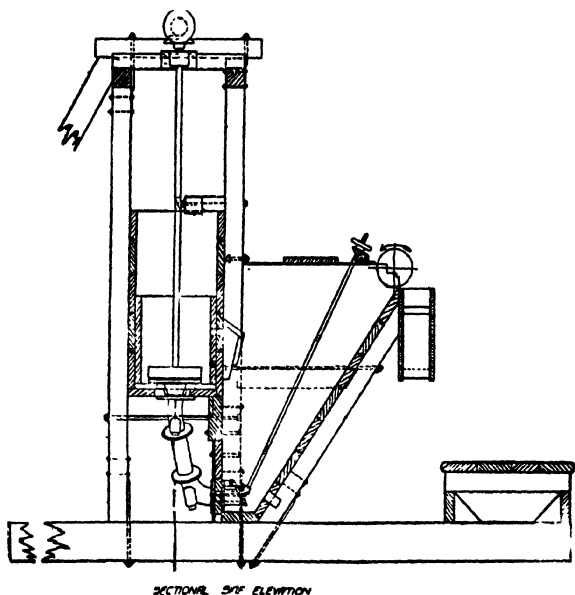
SECTIONAL FRONT ELEVATION

Minerals Separation, Ltd., London, Eng.

FIG. A.—FROTH FLOTATION PLANT

present time some 80,000,000 to 100,000,000 tons of ore are treated annually by this means.¹

By far the largest application of this process has been effected by means of the Mineral Separation machines,



Minerals Separation, Ltd.

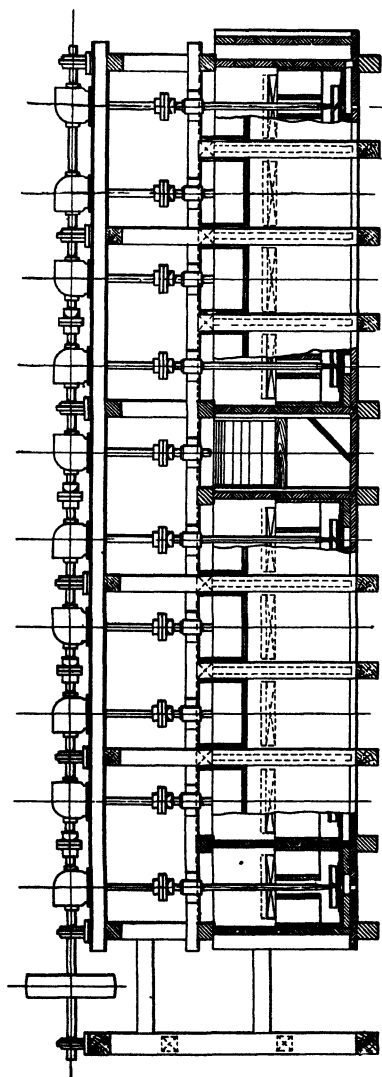
FIG. B.—FROTH FLOTATION PLANT

of which illustrations are given. Other types such as the Callow, K and K, Forrester, and Ruth, have been used widely.

In figures A and B a M.S. "Standard" flotation apparatus is shown in elevation and section; of late years, however, a modified design known as the sub-aerator type has been gaining preference.

¹ The U.S. Bureau of Mines reports that in 1926, 50,889,254 tons of ore were treated by flotation in the United States alone. (*Mining Journal*, 17th March, 1928.)

The standard machine will be seen from the diagram to consist of a long box, open at the top, divided into a series of compartments by vertical partitions. Each compartment is furnished with a vertical spindle capable of rapid rotation and fitted with cruciform impellers which just clear the bottom. To the front of the box, as shown in the sectional side elevation, is attached a second trough of triangular section ; this, similarly, is divided by baffles or vertical partitions into several compartments, and acts as a " spitzkast " for separating the mineral froth produced from the pulp introduced into it. A launder is fixed to the front rim of the trough separator to collect the overflowing mineral froth. Each agitation section communicates with the spitzkast compartment in front of it by a slotted opening, beneath the normal pulp-level, and from the bottom of the spitzkast a pipe connection, controlled by an adjustable valve, communicates with the bottom of the next agitation compartment, and so on ; the partitions in both agitation box and spitzkast-trough being arranged so as to direct the flow of pulp forward. The whole forms a series of alternate agitation and flotation units through which the ore-pulp continually passes. The crushed ore, made into a thin pulp with water, enters the first agitation compartment or mixing-box, where it receives the addition of a very small quantity of the " frothing-agent " : this may be a special oil or other substance capable of modifying the surface-tension of the water to the required degree and to produce a froth of sufficient stability. The amount of frothing agent required is extremely small, quite incapable in itself of influencing the specific gravity of the mineral to be floated ; it may vary from 2 lb. to as little as one or two ounces per ton of ore treated, or approximately to 5 tons of aqueous ore-pulp. With certain ores the water may



SECTIONAL FRONT ELEVATION

MINERALS SEPARATION LTD LONDON, ENGL.

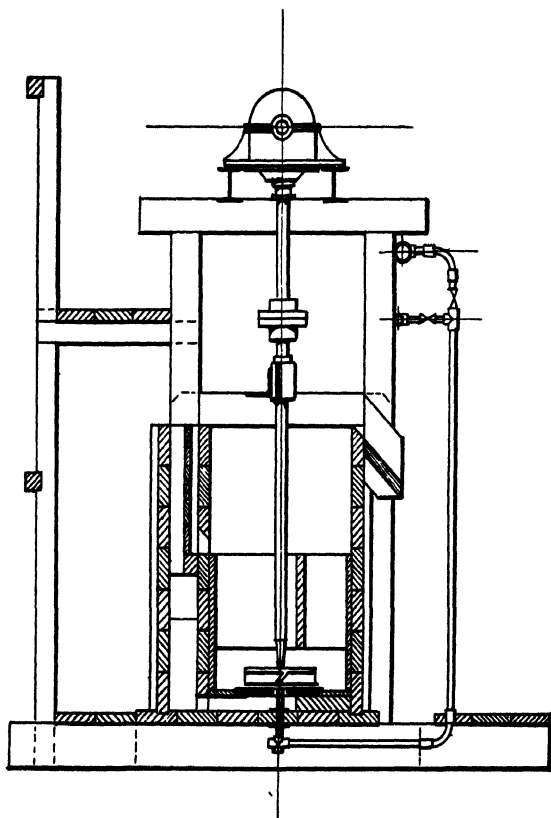
FROTH FLOTATION PLANT

FIG. C

be slightly acidified by a small continuous flow of sulphuric acid as it passes through the first mixing compartment.

The rapid rotation of each agitator within its rectangular compartment beats in large volumes of air churning the whole into a highly aerated pulp, which gives the frothing agent opportunity for bringing about the several physical reactions involved in the production of a mineralized froth. The pulp passes in a continuous stream from each mixing compartment, through the slotted opening beneath the water level, into its corresponding spitzkast chamber. Under the comparatively quiet conditions which here prevail such mineral as has already been brought into a floatable condition rises to the surface and collects as a froth, which is skimmed or floated into the collecting launder. The rocky particles with much yet unfloatable mineral fall to the bottom of the spitzkast, and are drawn by the pulp-flow and the suction induced by the succeeding agitator through the pipe connection into the next agitation compartment, where the pulp is again subjected to violent air-churning. Thence it again passes into the next spitzkast, yielding more mineralized froth and a settlement containing less mineral and proportionately more gangue. This cycle is repeated in each of the successive compartments through which the pulp travels until practically all the mineral has been yielded as a froth; the pulp-liquor, which now flows to waste, carries the gangue and such small amounts of mineral as may have escaped collection.

An eight-compartment box, capable of dealing with 600 tons of ore daily, with spitzkast, launders, shafting, and working space, etc., occupies an area of 30 ft. by 28 ft., requiring 14 ft. head room and about 65 to 70 h.p. for its operation.



CROSS SECTIONAL ELEVATION

MINERALS SEPARATION LTD. LONDON, ENG.

FROTH FLOTATION PLANT

FIG. D

With the progress of flotation treatment more exacting demands are now made on the process, not only with regard to yet higher mineral recovery but also in the separation of one sulphide mineral from another by "differential" flotation methods. Notable examples of this include the separation of galena from blende, blende from pyrites, and chalcopyrite and chalcocite from pyrites and pyrrhotite.

The machine found most suitable for this work is the subaerator, a recent design of which is illustrated in Figs. C and D. It will be seen to consist essentially of a row of agitation cells into which air is drawn through a pipe situated immediately beneath the impeller. The top zone of the cell is baffled, in this respect resembling the spitzkasten of the older standard type. The froth concentrate collects and is drawn off from the top of the cell while the water level is controlled by an adjustable weir which communicates with the bottom of the following cell.

The reagents required for successful flotation are chosen with regard to the composition of the ore to be treated and the results desired. They consist of various oils and in most cases certain chemicals which have a "modifying" effect on the component minerals and gangue.

A mixture of oils is usually employed, one of these being selected for its property of causing a pulp to froth when agitated with air, by preventing the too rapid coalescence of the small air bubbles: such oils are termed "frothers." The other is usually a thicker oil chosen rather for the purpose of imparting a minute film to the minerals it is desired to float; these oils are known as "collectors." Though nearly all oils possess both properties to some degree it is usually found better to use a mixture; the nature of this will vary

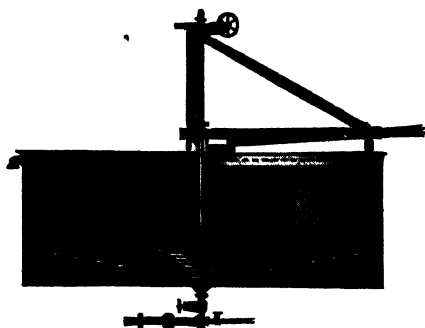
with the locality, the ore, the types of oil more readily available, and the individual experience or even preference of the operator.

The gangue modifying agent is usually an alkali such as soda ash, caustic soda, or sodium silicate ; its effect is to cause the gangue and oxides to be more readily wetted and to remain sunken. Acid, formerly used for the purpose, is now seldom employed. Other chemical reagents ("accelerants" or "depressants") may be used to enhance or hinder the flotation of specific minerals according to the nature of the differential separation required. Thus, sulphate of copper is used to aid the recovery of zinc blende after a galena product has been floated. Soluble sulphides may be used to sulphidize the surface of certain oxidized copper or lead minerals and thus to render them floatable. The addition of a very small quantity of an organic preparation known as "*Xanthate*" is now widely practised. It has the effect of enhancing recoveries and of producing a dryer and more coherent mineralized froth.

The amount of oil required may vary from $\frac{1}{4}$ lb. and perhaps less per ton of ore to as much as 2 lb., while the chemical reagents may range from similar small amounts up to as much as 10 lb. per ton of ore in exceptional cases.

For concentration of tailings or slimes by flotation it is important that the pulp should be of suitable consistency, that commonly found desirable being in the proportion of about one part of solid to from four to six parts of water. As the pulps from the mill are usually more dilute than this they must be thickened before being fed to the flotation plant and the surplus water rejected. For this purpose "thickeners" are used; that most generally adopted is the "Dorr Continuous Thickener"; this consists of a circular tank provided with slowly revolving radial arms, fitted

with blades set at such an angle as to move the settled and thickened pulp towards the centre. The thin pulp is fed in near the middle of the full tank, just below the surface, so as to cause little or no disturbance to the bulk of the liquor to be settled. The thickened pulp is discharged at the centre of the bottom of the tank while the clear water overflows at the circumference. This and other types of thickeners are used for many similar metallurgical purposes.



Dorr Cyanide Machinery Co , Denver, U.S. A

DORR CONTINUOUS THICKENER

The illustration on page 34 shows two of the flotation units recently installed at Anaconda ; on each side of the central gangway are the spitzkast-trough compartments, each with its regulating valve which controls the pulp delivery to the next agitator of the series. The agitation compartments are behind, with enclosed gear boxes to each spindle ; the collecting troughs or launders for the removal of mineralized froth are nearest to the gangway, and revolving skimmers to aid in the withdrawal of the coherent froth from the lip of the spitzkast-trough are clearly visible on the left.



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Minerals Separation Ltd., London, Eng.

FROTH FLOTATION PLANT (ANACONDA)

To illustrate the magnitude of flotation treatment, we may cite a few of the larger plants which are in operation in the United States.

The Inspiration Mine has a plant of 20,000 tons daily capacity, though not at present operating on full tonnage. A recovery of 94% of the copper in sulphide form is made from an ore containing 1.1% Cu.

The Utah Copper Co. has two flotation plants of a total capacity of 50,000 tons per day. The Butte and Superior Co., dealing with a more zincy ore milled in one year 625,500 tons, producing 137,000 tons of flotation concentrates. The Calumet and Hecla Mines are successfully operating a flotation plant for the recovery of native metallic copper.

In other countries the Braden Copper Mine (Chile) operates a plant of 12,000 tons daily, with a recovery of upwards of 90% of the copper occurring as sulphide.

The most noteworthy example of the flotation of oxidized copper ores is seen in the Belgian Congo, where a plant is in operation on an ore which contains its values wholly in an oxidized form. This plant is in course of enlargement to 3,000 tons daily.

Whatever system of concentration, or variation or combination of systems, be employed the ores, except such as are rich enough for direct smelting, necessarily require crushing. The machines utilized for crushing are not peculiar to the treatment of copper ores, the same types being employed for those of other metals. Unless flotation be the method of concentration adopted the aim is to avoid the production of any substantial proportion of slime mineral, and for this reason stamps (such as are used in gold-ore milling and in the reduction of Cornish tin-ores) are not commonly used. The Lake Superior ores supply an example of such stamp-battery crushing, but here the copper is present in the metallic



The Hardinge Conical Mill Co., New York

HARDINGE CONICAL MILL

form ; after hand-picking the ore is crushed by steam stamps to about $\frac{1}{2}$ in. size, this being followed by jigging and tabling. Latterly regrinding of the tailings in "Hardinge" mills has been adopted, prior to their flotation treatment for values previously lost.

In the preparation of the ore the first or coarse crushing is effected by means of gyratory cone crushers or jaw crushers of the Blake type. The intermediate crushing is performed by roll- or disc-crushers, and the final wet reduction effected by means of ball- or rod-mills, which are usually arranged to work in closed circuit with a drag classifier. By this arrangement the classifier returns to the ball mill the ore which is insufficiently crushed, while the water-solid ratio is maintained in the classifier at a density which ensures the overflow of ore of sufficient fineness from the classifier into the flotation circuit. The load which thus circulates through the ball-mill and classifier is three or four times the tonnage fed to the plant. The better-known types of modern fine grinding mills are the Hardinge Conical mill, Marcy rod mill, and the Allis-Chalmers granulator.

The illustration shows the Hardinge Mill. The effect of its conical shape is automatically to keep the largest balls at the greatest diameter of the mill where the maximum grinding effect is required ; as the partly crushed ore approaches the discharge end the smaller balls complete the grinding to the desired degree of fineness. The ultimate size is regulated by the weight of balls and the speed of rotation of the mill. If required the whole of the product may be reduced to slime, or, on the other hand, a fine granular sand may be produced with the minimum of slime. The material to be crushed is charged into the mill through the scoop feed shown on the left, the discharge taking place through the hollow trunnion on the right.

CHAPTER III

ROASTING

THE preliminary crushing and concentration treatment having produced the enriched mineral products of various grades and metal contents, we have now to consider their further treatment.

Broadly speaking, smelting processes may be divided into two classes according to the type of furnace used—

(a) blast furnace, and

(b) reverberatory furnace methods.

Both types of operation primarily result in a further concentration, the molten products being “matte” and “slag.” The former carries nearly all the copper, while the latter contains the barren material present in the original concentrates or formed by the “flux” added to facilitate slag formation. Matte is essentially a mixture of sulphides of copper and iron, and in whatever way it is produced has to pass through a further process before the metal is reached. Whether the blast or reverberatory furnace be employed the object sought is the same, viz., the collection of the copper into a small amount of matte, the barren material being converted into a fusible slag by the addition of suitable fluxes. Only in rare instances does it happen that the ore is what is termed “self-fluxing,” that is, where the composition of the barren rock permits of its fusion into slag unaided by additions, under the conditions of furnace temperature usually available. Further, in most sulphide ores or concentrates the proportion of sulphur is too high to allow of immediate

smelting. As will be explained later, the presence of sulphur in undue amount involves the production of a large amount of matte of low value, whereas the chief desideratum is a small amount of richer material (i.e. greater concentration). It is therefore usual to remove a portion of the sulphur by "roasting" before proceeding with the smelting operation proper.

Roasting.—This is carried out in different ways according to circumstance. In some cases *heap-roasting* is practised, but more commonly mechanical or hand-worked furnaces, of various types, are used for the purpose.

Heap-roasting was the earliest method for partial sulphur elimination, and this process for rendering sulphide ores available for smelting was probably discovered through the accidental ignition of a pile of sulphide mineral. Though still used in some localities it is nearly obsolete, having given place to more sanitary methods involving the employment of furnaces from which the sulphurous gases can be turned to use in the manufacture of sulphuric acid, or discharged through a high stack into the upper air.

The construction of a "heap" requires skill and judgment, the aim being to remove all sulphur in excess of the amount required to form matte in the subsequent smelt. Should the roasting operation be carried too far the deficit of sulphur can be corrected later, by the addition of "green" (unroasted) ore to the smelting furnace. A sound floor of stone or slag is first prepared, on which is placed a layer of fuel. The ore is spread upon this, larger pieces being laid first and smaller pieces placed above them; finally, the heap is covered with fines. Chimney-ways are left at intervals in the heap to promote draught, which must be carefully controlled to prevent overheating

and the consequent danger of sintering. According to Peters¹ a heap "40 ft. long, 24 ft. wide, and 6 ft. high, will contain about 240 tons and burn seventy days." The same authority, who gives an exhaustive account of the operation, states that the best average height for ordinary ore is 7 ft., the time being increased or diminished by ten days for every 6 in. added to or taken from the heap.

As practised at Mansfeld (Germany) heap-roasting has a different object. The copper-bearing schists here contain a proportion of bituminous matter which it is desirable to remove before smelting, and the schist being self-burning no extraneous fuel is required.

Stall Roasting.—This modification of heap-roasting is conducted in stalls or rectangular brick chambers, the front wall of which is not permanent but is built up as a "dry" wall with the necessary air-holes to control the burning. The stalls may be provided with a system of flues leading to a stack, or may discharge the gases into the open air; otherwise the conditions governing their use are similar to those of heap-roasting. The stall method possesses one important advantage in the opportunity afforded by the permanent floor for collecting and saving any copper salts which may be dissolved and washed from the heap by rain.

Roasting Furnaces.—In most works of limited output hand-worked roasting furnaces are employed, not only for roasting (or calcining) ore and concentrates but for the roasting of the matte obtained from subsequent operations. The furnace consists of a long rectangular hearth with a fireplace at one end, divided from the working hearth by a bridge over which the flames from the fire pass. It is covered with an arched roof extending over the whole length, a stack being provided at the

¹ *Modern Copper Smelting*; 7th Ed., p. 108.

end remote from the fire. Working doors are arranged upon one or both sides of the furnace according to the width of the hearth. The ore to be calcined is fed into the cool end of the furnace in successive charges, and is gradually moved towards the fire end by paddles or "rabblers," operated through the working doors. The hearth is divided into sections—usually four in number—which may be stepped slightly one above the other, or the division may be by imaginary lines. In normal working a finished charge which has been gradually moved forward till it reaches the bridge end is withdrawn from the furnace, the charges still in course of working on each hearth-section being similarly brought forward one step, and a fresh charge of raw ore fed to the first section.

The size of the furnace will vary with the class of ore to be roasted; the richer the ore in sulphur, the longer the hearth required, up to a maximum length of about 60 ft., a condition being that the furnace heat at the far end must still be strong enough to ignite the sulphur in the ore there introduced. Furnace-width is limited by the distance over which the rabbling tools can be efficiently handled; in the United States, furnaces as wide as 16 ft. are used, but in Europe this measurement rarely exceeds 12 ft., and is frequently less.

In roasting pyritic ores rich in sulphur but little additional heat is required from the grate, which is therefore small in area compared with the hearth, the chief supply of heat being derived from the oxidation of the sulphur and iron. In extreme cases, the ore, once ignited, may require no further external heat: such conditions rarely obtain in hand-fired furnaces, but they are occasionally available with mechanically operated calciners wherein the heat is better conserved. The output also varies with the class of ore and the

size of the furnace ; a large American hand-calciner will treat from 10 to 12 tons of ore per twenty-four hours.

The roasting operation is not continued until all the sulphur is oxidised (as it is, for example, in the case of zinc ores), as some sulphur is still required for the production of matte (see page 72), the amount and richness in copper of the latter depending in part on the proportion of sulphur it contains. The effect of too large a proportion of sulphur has already been referred to ; conversely, a shortage of the element will lead to a small yield of high-grade matte ; this latter result, though not undesirable from some aspects, involves a greater loss of copper in the slag simultaneously produced. In typical cases the calcining of the ore is satisfactory when the finished material still carries from 5% to 7% of sulphur.

The simple form of hand-roasting furnace has been modified in various ways. For example, two or more hearths may be superposed, a device which conserves heat, the flame passing over one hearth after another in series, thus leading to further economy in floor and roof area. Another type is the muffled furnace, wherein the gases from the fire are prevented from coming into direct contact with the ore by the interposition of a protective arch covering the latter, the heat being radiated through the arch. The working hearth may also be heated through the bottom by passing the flames beneath it ; furnaces of this class are used where it is desired to collect the sulphurous gases for the manufacture of acid. In many districts such collection is compulsory, as the gases have a detrimental effect on surrounding vegetation.

Mechanical Roasters.—Roasting ores by hand-labour is a tedious operation, and its successful accomplishment depends on the skill and care of the workmen engaged,

the expense being high in relation to the output obtained. To overcome this objection many successful furnaces have been designed to replace hand-rabbling by mechanical contrivances. Satisfactory roasting calls for the continuous "rabbling," or turning of the ore, so as to expose fresh surfaces to the action of the air. This can only be done intermittently by hand, as the labour is considerable and periods of rest are necessary for the men ; and further, the constant opening of the working doors tends to cool the furnace. Mechanically worked furnaces not only reduce the labour and general working costs, but yield a more uniform product. Many varieties exist which cannot here be referred to in detail, only those being selected for brief mention which illustrate the more common types.

The Bruckner Furnace.—This is essentially a revolving cylinder lined with brick, and fitted with an independent firebox at one end. The cylinder, mounted on rollers, is caused to turn slowly whilst the heat from the grate passes through the interior ; each revolution gradually and thoroughly turns over the whole of the charge, exposing it to the furnace gases and heated atmospheric oxygen. This type is not now in common use, partly on account of dusting losses.

Of a different type are the *Brown-O'Hara*, the *Brown "Horseshoe,"* and the *Pearce "Turret"* furnaces. In these, rakes are moved through the ore, by chains or other means, to secure the necessary turning and exposure to oxidation of the ore charges. In another class are the circular furnaces of the *Brunion* type, in which the hearth and its charge revolve in a horizontal plane whilst the rakes are stationary.

The McDougal Furnace is the most commonly used in America ; at the time of the author's visit to the great "Washoe Smelter" at Anaconda, Mont., no less

than fifty-six were employed at this works alone. They were also in use at the "Highland Boy Smelter" at Murray, near Salt Lake, for treating ore containing about 35% sulphur (and 3.4% copper), which was reduced to 7% or 8% S. The latter instance affords an example of roasting without the use of extraneous fuel. The McDougal roaster contains several—usually six—circular hearths, placed one above the other, each being furnished with a set of rabbles or ploughs fixed upon a radial arm which is attached to a central revolving shaft. The ploughs are set at an angle so as to cause the ore to travel to or from the centre on alternate hearths, the ore dropping from one hearth to the next through holes provided for the purpose; the travel of the ore is from the periphery to the centre of one hearth, whilst on that next below the ploughs are set to convey in the reverse direction. The furnaces are built in various sizes, those at Highland Boy having six hearths, each 14 ft. in diameter. The wear on the rabbles is considerable, but is checked by a system of water cooling, the arms being hollow to permit of a constant current of water passing through them. At the above works the amount of water consumed amounted to 40 gallons per minute, in furnaces having a capacity of 35 tons per day for the ore mentioned. Cooling by means of a current of air is now usually adopted, as this is beneficial in promoting oxidation, the heated air after cooling the rabbles being allowed to escape into the furnace.

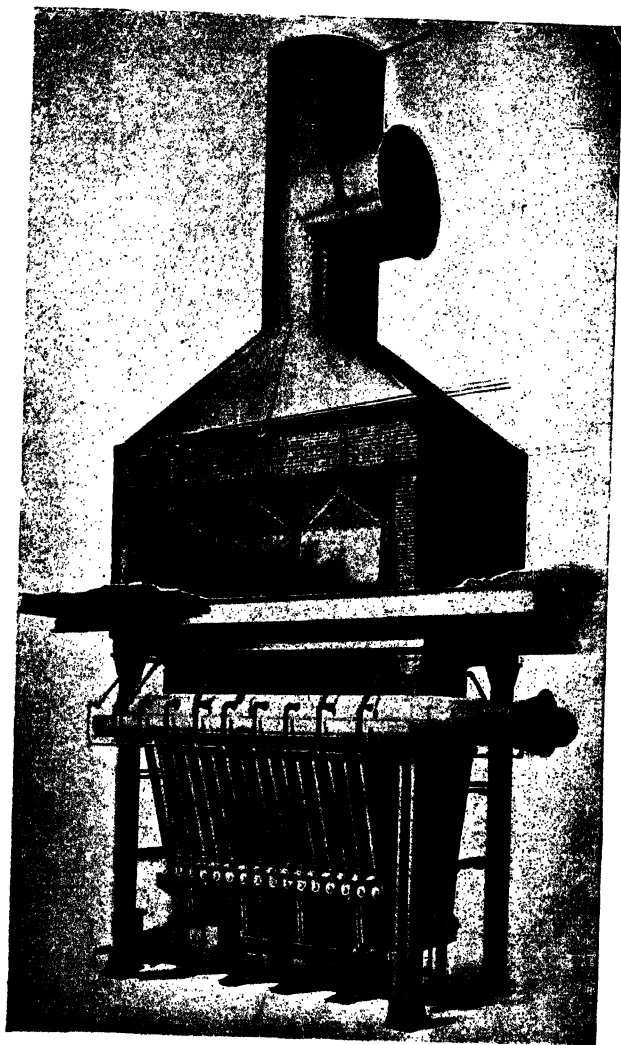
The "*Wedge*" is another well-known furnace of the same general type, but possessing various modifications in detail. One feature consists in bolting the rabble arms to a hollow central shaft, through the interior of which they can be approached for replacement when necessary without cooling the furnace.

CHAPTER IV

THE BLAST FURNACE

UNTIL recently, the blast furnace has been more extensively used than the reverberatory in the production of matte. Latterly, however, mainly owing to the increasing production of flotation concentrates, the blast furnace has been superseded in most large installations by the reverberatory, a type of furnace more suited to smelting a charge consisting almost wholly of fine material. The blast furnace, on the other hand, is especially applicable for the smelting of coarse ore carrying but a small percentage of fines, as any substantial amount of the latter will prevent the free passage of the air through the charge and result in irregular working. Moreover, the fines are largely blown out prematurely, by the forced draught as flue dust, which must be settled in collecting flues and dust-chambers prior to re-handling for the recovery of their metal contents. The difficulty of smelting dry slimes and flue dust in the blast furnace is to some extent overcome either by briquetting or "sintering" them. The former method though cheaper is inefficient, as many of the briquettes again disintegrate into dust in the upper region of the furnace. In sintering processes the particles are first partially fused into a clinker-like product by the action of heat, and a current of air passing over or through the material. The practice of sintering concentrates, etc., will tend to revive the use of the blast furnace, since the physical condition of the sinter renders it suitable for smelting in this type of furnace.

Blast furnaces differ widely in shape, size, and horizontal section, which latter may be round, oval, or



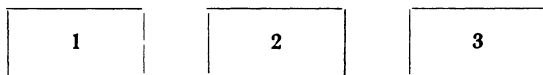
The Allis-Chalmers Co., Milwaukee, U.S.A.

WATER-JACKET BLAST FURNACE

rectangular ; the last named is the most commonly adopted, and employed almost exclusively where a large output is demanded. A furnace of this class is shown in the accompanying illustration.

In the early days of blast furnaces brick construction was used, and these furnaces still survive in a few places where special circumstances justify their continuance ; but they are now almost entirely superseded by the modern water-jacketed furnace.

In later years the size, and therefore the capacity, of water-jacket furnaces has increased enormously ; from a charge of 50 tons per day, they have developed gradually to a maximum of not less than 3,000 tons per twenty-four hours, though as a rule a number of smaller units is preferred to one of such extreme capacity. The example quoted is the Mathewson furnace at the Washoe Smelter, Anaconda, Mont. This was developed from three smaller furnaces originally arranged in a line as shown in the diagram in plan—



The first step was to remove the adjacent end walls of Nos. 1 and 2, the intervening space being filled by joining up the longitudinal walls, thus converting the two furnaces into one. Later No. 3 was joined in similar manner to No. 2, giving a total length of no less than 87 ft., the width of course remaining the same as the original furnaces, namely, 54 in. at the tuyère (or forced-air inlets) level. The use of this furnace was discontinued after 1918, but its historic interest remains.

The water-jacket possesses many advantages over the brick furnace, among which may be mentioned simplicity in erection, greater ease in working, and ready accessibility for repairs ; whilst slag of any desired

composition can be made without affecting the jacketed steel walls. Practically the only disadvantage that can be urged is the heat lost in the cooling water. This has been variously estimated, and may be taken as from 7 to 10% of the heat produced by the coke burnt in the furnace. A supply of clean water is necessary to prevent undue deposition of solid matter in the jackets, though this difficulty is overcome in great measure by the provision of hand-holes and draining taps at the bottom of the jackets.

The detailed drawing given is that of a modern matte-smelting furnace designed by W. A. Heywood, and constructed by the Allis-Chalmers Co., of Milwaukee, U.S.A. It consists of a ribbed cast-iron bottom-plate supported on eight screw-jacks. From this rise the steel water-jackets, the lower ends of which rest within flanges on the edge of the bottom-plate. The upper jackets are suspended from I beams (at the feed-floor level) which rest upon the main supporting columns and also serve to carry the brick superstructure. The jackets are fitted with a system of piping for water circulation, cold water entering at the lower level of the jackets, the heated water discharging in a continuous stream at the top into a funnel. The discharge, and consequently the circulation of the water, being easily observable, any accidental stoppage of the flow can be attended to before damage arises. The furnace is provided with twelve forced-air inlets or tuyères, spaced 12 in. between centres on each of the long sides. The furnace ends are also jacketed but not provided with tuyères.

The spout through which the melted products escape is water-cooled and is set at an incline, the edge of the lip being above the level of the top of the discharge hole in order to trap the air and prevent it from blowing

out at the discharge. The furnace, when working, is full of molten material up to the lip of the spout, from which is a continual overflow of matte and slag into the "settler" (see page 58). The flow may be continuous or intermittent, depending upon the rate of smelting. When intermittent discharge is practised there is a break in the jacket continuity, the space being built in with brick-work, in which a "tap-hole" is provided. The latter is plugged with clay, which is pierced from time to time by driving an iron bar through it, thus providing an opening—for the discharge of the molten products—which is re-plugged at the conclusion of the "tap." The furnace is charged with the ore, coke, and flux at the feed-floor, through counterbalanced sliding doors.

Blast furnaces are usually described by their dimensions in plan at the tuyère level, the one referred to above being a 42 in. $\times$ 144 in. The interior walls exhibit a uniform straight line from the top of the jackets to the bottom plate, there being nothing to hinder the free fall of the charge in the furnace. In this respect designs vary; in some cases the upper jackets are vertical for a short distance, the next lower set then inclining inwards to the tuyère level, whilst the bottom jackets are again vertical. The air-blast is provided by blowers, usually of rotary type, the pressure varying according to the depth and nature of the ore charge, from 30 to 40 ounces per square inch being common practice. One form largely employed is the well-known *Roots'* blower, and in the same class is the *Connersville*, also extensively used.

The function of the blast furnace in matteing is, in reality, to secure a further concentration; it does not complete even the separation of the sulphur and the iron, nor produce metal, but concentrates the copper



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BLAST-FURNACE FEED FLOOR

contents into a smaller bulk (relatively to the weight of concentrated ore from which it is derived) by rendering the whole ore-mass molten, and separating the heavier matte from the lighter rock matter. To bring about the fusion heat must be supplied, partly by the addition of fuel, and partly by the oxidation of the mineral sulphides in the ore charge. In certain cases the major part of the heat is derived from the latter source, only a very few per cent of fuel being added. When this condition obtains, the operation is known as *pyritic smelting*, which will be more fully referred to later.

It has been shown in the chapter on roasting that oxidation of pyrites produces heat, and wherever such oxidation takes place the same heat effect results, whatever the type of furnace employed. In the majority of cases, however, some additional heat is required for blast furnace smelting, independent of the heat-generating substances in the ore. Coke is the fuel almost invariably used for this purpose, and should be of good quality as regards mechanical strength, as it has an important duty to perform in addition to the supply of heat, namely, to withstand the weight of the column of ore charge and to keep this open, thus permitting free passage of the air-blast. The coke should be of low ash-content, for not only does the ash proportionately detract from its heating value, but requires the addition of flux to render it fluid and miscible with the general mass of the slag.

The amount of coke will vary with each individual ore and with the size of the furnace, but, generally speaking, the larger the furnace the less the coke required, as heat radiation-loss diminishes with increase in furnace capacity. In average practice when treating low-grade ores the consumption of coke may be taken as from 10% to a maximum of 20% of the weight of the

charge, but the required quantity may be calculated fairly closely. For this purpose, it is necessary to know the "calorific value" of the coke (i.e. the number of "heat-units" which each pound will generate), and upon the same side of the balance sheet we must place the heat-units generated by oxidation of pyrites. On the debit side of the account will be the heat which must be supplied: (a) for driving off moisture and carbonic acid from the charge; (b) for that carried away by the molten slag and matte; (c) for heat lost in the escaping gases, and in the flue-dust mechanically blown out of the furnace; (d) for heat lost in the hot water escaping from the water-jackets; and (e) for loss by radiation. The chief elements of difficulty in arriving at an exact balance are: (1) The uncertainty of how much of the carbon in the coke will be burnt to carbon monoxide and how much to carbon dioxide; (2) the amount of mineral sulphides that will be oxidized; and (3) the radiation figure. This last item is usually arrived at by difference after all the more easily determined factors are calculated, a margin being allowed to satisfy this demand.

An example of a heat balance sheet is quoted¹ at the top of page 53, the heat units being expressed in terms of horse-power.

In this instance, however, the blast was pre-heated in a stove, as in iron smelting practice, a procedure now rarely adopted in copper smelting.

Various means have been tried for utilizing the waste-heat in the slags and gases but no generally successful scheme is in operation. In an apparatus devised by Vautin² the slags are granulated in a boiler of special design, producing low pressure steam which drives a low-pressure steam-turbine. Though this method gave

¹ *Mineral Industry*. Vol. XI, p. 691.

² Eng. Pat. 3623. 1909.

	Theoretical Horse- power.	Practical Horse- power.
PRODUCERS—		
1. Oxidation of pyrite . .	3,416	427
2. Oxidation of coke . .	5,153	644
3. Heat in blast	1,652	206
	10,221	1,277
CONSUMERS—		
1. Expulsion of CO ₂ . .	1,700	212
2. Expulsion of water . .	334	42
3. Jacket water	2,440	305
4. Slag	3,060	383
5. Matte	190	24
6. Flue dust	28	3
7. Escaping gases	1,042	130
8. Water in blast	738	92
9. Radiation	689	86
	10,221	1,277

satisfactory results on a large experimental scale with slags from iron smelting furnaces, it does not appear to have been adopted. The following calculation shows the amount of power that theoretically could be derived from copper blast furnace slags based on the amount of available heat.

By experiment, it has been found that one kilo of slag holds from 318 to 350 calories¹ of available heat. Taking the lower figure—

1,000 kilos × 318 calories . . .	318,000 calories.
From this deduct the heat carried away in the quenched slag—	
at 100°C. 1,000 kilos × 100°C. × .18	
(specific heat) =	18,000
and say, 10% moisture = 100 kilos	
× (100° - 16°) =	8,400 26,400 calories.

Actual heat available

291,600

¹ The heat required to raise the temperature of 1 gramme of water by 1° Centigrade.

Allowing 25% loss, there are still available 218,700 calories for water evaporation ; this, divided by 537 (the latent heat of vaporization) plus 85 (the water being originally at 15°C.) = $\frac{218,700}{622}$ or 351.6 kilos of steam.

Taking the efficiency of the apparatus at 80%, there are 281.3 kilos of clean steam available for the turbine, and assuming a steam consumption of 14 kilos per h.p., 20 h.p. would be produced per 1,000 kilos of slag.

CHAPTER V

PYRITIC SMELTING

THIS term applies to a modified form of blast furnace practice wherein ores rich in copper-bearing iron pyrites ("pyritic" mineral) and with free silica as gangue material are smelted by the heat derived mainly from the oxidation of the iron and sulphur of the mineral. The advantages of the process, where applicable, are twofold, viz., in saving the preliminary roasting as well as in reducing the amount of coke required in the blast-furnace. The method was first proposed by John Hollway, who pointed out that the compact Rio Tinto pyritic sulphides should be capable of being smelted by the heat derivable from their own oxidation. In Tasmania, at a later date, Robert C. Sticht developed the process and treated the pyritic ores of Mount Lyell in this manner with considerable success. A further example of its efficient operation is to be found at the works of the Tennessee Copper Co., where it was worked out under the superintendence of W. A. Heywood. Given an ore containing sufficient sulphides and a suitable amount of free silica to combine with the oxide of iron produced, no coke or other added fuel theoretically should be needed, as the oxidation of the pyrites to sulphur dioxide and ferrous oxide, and the combination of the latter with the silica, develop enough heat to perform the smelting operation. In practice, however, a small percentage of coke is added, though this may not exceed 3% to 4%, and in some cases even less. Thus at Rio Tinto, owing to the favourable character of the ore, only 2% to 2½% of coke is required, whilst

at the Tennessee Copper Company's smelter it has been reduced to 1.9%. Even here its function is less as a heat producer than as an assistance in keeping the charge "open," and in correcting any local lack of heat or other irregularity which may develop in the furnace. Thus if a mass of partially fused silica tends to form in the upper zone of the furnace (which, if allowed to grow, would eventually choke the draught and stop the operation) it can be "barred-down" on to a layer of coke placed to receive it, where, with the addition of some more basic charge, the temporary heat supplied by the coke smelts and removes the obstruction.

Although pyritic smelting, strictly speaking, means an operation where coke consumption is reduced to an almost disappearing limit, and though a furnace may smelt "pyritically" for several days on end, it is more usually necessary for one or other reason to exceed the theoretic pyritic smelting fuel proportion. Where it is the practice to add a small but regular amount of coke the term "partial pyritic smelting" is used to describe the operation. There is no fixed border line between "pyritic" and "partial pyritic smelting," but the expressions are generally well understood.

Mention has been made for the need for free silica as a slag-forming constituent in pyritic smelting; without it, indeed, the process could not be carried out. If the gangue matter were composed solely of *silicates* (that is, of gangue minerals in which the silica is *already* combined with a base), these would not supply their quota of the necessary heat (by the chemical union of "acid" silica with base) but would also require extraneous heat to melt them. The oxidation of pyrites alone would not supply sufficient for this purpose, its margin of available heat being comparatively small. For this

reason pyritic smelting is not applicable to ores rich in silicates of alumina, and any attempt to carry more than 10% of alumina (Al_2O_3) in the slags would result in failure. It is, however, a process adaptable to a large number of ores, provided that they contain sufficient sulphur and iron. As to the lower limits of iron and sulphur, probably a minimum of 20% of the latter is necessary; this, if all in the form of FeS_2 , would be equal to a content of 37% of pyrites. At Mt. Lyell¹ in treating ore carrying 2.15% to 2.25% copper, 95% to 96% of the iron accompanying it as sulphide is oxidized, and the resulting matte contains 45% of copper, the coke consumption being from 3% to 4%. The slags contain from 36% to 38% of silica (SiO_2), 45% of ferrous oxide (FeO), some lime, and about 7% of alumina (Al_2O_3). A concentration of the copper from 20 parts of ore into 1 part of matte is obtained, and at this high ratio the slag contains from 0.35% to 0.45% copper.

At one time it was considered necessary to employ a hot air-blast in pyritic smelting, but though the practice may still survive in a few cases it is now generally held that a cold blast gives the best results. The air pressures used are high, e.g. at Mt. Lyell, where the ore column reaches 18 ft., a 64-oz. blast is employed. The amount of air required is necessarily considerable, as nearly all the iron and most of the sulphur must be oxidized if a high-grade matte is to be made. A reduction in the quantity of air would naturally result in oxidizing less of the iron pyrites, thus producing a lower grade matte by dilution with unoxidized ferrous sulphide; an increased proportion of sulphides in the charge without a corresponding increase in air supply will, of course, produce the same effect.

¹ *Pyritic Smelting Bull.* (Amer. I.M.E.), April, 1915.

Pyritic smelting is sometimes conducted in two stages. In the first smelt, a low-grade matte, which may contain from 10% to 30% copper is produced, with, as a rule, clean slags. This matte is then concentrated in a second operation to 40% or more of copper, by re-smelting with silica, circumstances and conditions determining the best method to employ. Pyritic smelting is specially suitable for the treatment in the blast furnace of heavily mineralized pyritic ores, whose copper values cannot be raised effectively by concentration. The reason for this is that such ores usually contain comparatively little gangue matter in proportion to sulphide, and previous concentration at best could only reduce the material to be smelted by a relatively small amount. Thus, one carrying 33% of sulphides could only be concentrated in the ratio of 3 to 1, even supposing perfect concentration were possible.

Settlers.—The molten products, matte and slag, whether derived from pyritic or ordinary smelting, are discharged from the blast furnace into a "settler," wherein separation of the two takes place by virtue of their different specific gravities. The old form was a rectangular truck or box running on rails in front of the furnace, but these have been replaced by fixed settlers of large capacity, reaching 15 or 16 ft. in diameter and 4 or 5 ft. in depth, built of $\frac{3}{8}$ to $\frac{1}{2}$ in. steel plates riveted together. They are lined with refractory brick of basic composition, chromite forming the best material where low-grade matte is produced. The bottom is lined with 14 in. and the sides with 9 in. brick; a 2-in. space is left between the lining and the plate, which is filled with coke-breeze or other non-conducting material. A coil of perforated water-pipe surrounds the settler to permit of cooling the outside if necessary. It is usual to provide expansion joints in the brick-work

by inserting a $\frac{1}{2}$ in. strip of deal between each fifth brick vertically and each sixth brick horizontally.

The heavier matte is tapped from time to time into ladles for removal to the converter from near the bottom of the settler, while the lighter slag continually overflows at the lip, either into cars for removal to the dump, or into a stream of water in which it is granulated and washed away down a launder. The constant flow of molten slag from the furnace prevents its solidification (or "freezing") in the settler, and the mass is further protected from chilling by the crust of frozen slag which forms a roof over the molten material below.

According to tests by F. E. Lathe,¹ two or three smaller settlers in series yield a cleaner slag than does a single one of larger diameter.

¹ Metal loss in Copper Slags; F. E. Lathe. *Eng. & Min. Journal*. Vol. C, p. 306.

CHAPTER VI

BLAST-FURNACE PRODUCTS

THE products of the blast furnace are matte, slag, flue-dust, and gases, the last named being in most cases a waste product, consisting mainly of nitrogen, sulphur dioxide, some sulphur trioxide, carbon dioxide and monoxide, and a small amount of unburnt oxygen. The gases also carry away in suspension the finest ore-particles that have escaped settlement in the interposed flues and dust-chambers, as well as varying amounts of zinc, lead, arsenic, and antimony vapours, if these elements be present in the ore smelted. Such gases are frequently the cause of trouble to the owners of surrounding land, owing to their destructive effect on vegetation; for this reason, several large concerns have found it necessary to install their smelting works in districts removed from centres of population or agriculture, even though the mines may be located there. Where this is impossible the neighbouring agricultural land is sometimes bought by the operating company, or suitable arrangements are made with the parties affected. In certain localities the law requires the gases to be collected and neutralized; thus, when smelting rich pyritic ores, the sulphurous gases may be used for the manufacture of sulphuric acid, after separation of flue dust. In most cases, however, the gases are too poor in sulphur or there is no market sufficiently near for the acid produced. As the compulsory condensation of sulphur gases to acid involves the sale or utilization of the latter, it has sometimes led to the introduction of a subsidiary industry attached to

the smelting works. An example of this is the manufacture of superphosphate for agricultural purposes. No market for sulphuric acid being available, natural phosphate rock is imported and converted by the acid into the assimilable superphosphate, a valuable artificial manure. The smelter, so often harassed by the agriculturist, may thus become his useful ally. Acid is being produced directly from blast furnace gases at two large smelting works in Tennessee, where heavily pyritic ore is treated; in rarer instances, such as in the smelting of cupriferous schists at Mansfeld, Germany, the gases after washing, which contain as much as 22% of carbon monoxide, are collected and used for driving gas-engines for the supply of power to the works.

Blast-furnace Slags. The proportion of the various constituents forming the gangue or waste portion of the ore is rarely such as will yield a satisfactory slag on smelting (in other words, to be "self-fluxing"), hence an addition of either base or silica must be made in order to produce a sufficiently fluid slag at the temperature available. In most cases silica tends to predominate in the gangue, and therefore a base, such as oxide of iron or lime, or a mixture of both, is needed to flux it. Mansfeld, in Germany, is an exception; here no fluxes are added to the heap-roasted schist, though a certain amount of basic slags from other operations is included in the charge, mainly with the object of recovering their copper contents, but incidentally, to assist in the furnace running. Again, certain copper ores in Chile possess a gangue of garnet-rock containing lime, iron, and silica in such proportions as to be self-fluxing; but these examples are comparatively rare. It is clear that it will be undesirable to add barren flux if it can be avoided, for not only is the cost of such flux involved, but heat

must be supplied to melt it, whilst the additions necessarily add to the amount of slag produced, every ton of which carries some copper to waste ; finally, any excess of slag takes up space in the furnace which should be occupied by more valuable material. Accordingly, when circumstances permit, ores rich in bases are mixed in due proportion with others rich in " acid," or silica, the one supplying the deficiencies of the other. This plan is adopted as far as possible by " Custom " smelters who deal in purchased ores, but is often impossible in works whose supply of ore is limited to one or two mines. The greater the amount of gangue material—usually silica—to be slagged, the larger, naturally, will be the amount of fluxing base required, and as this increases the cost of the operation it is obviously desirable to remove as much as possible of the gangue in the preliminary concentration steps. As, however, these necessarily involve some loss of copper in the tailings, they must not be carried too far ; each ore must be separately considered and its treatment adjusted to yield the maximum of profit. Hence it happens in practice that large quantities of gangue still remain to be removed as slag in the furnace.

In deciding upon a slag composition, the following considerations should be taken into account—its formation-temperature must not be too high, and its melting point must be reasonably low. Formation temperature and melting point are not identical, some slags requiring a high degree of heat *to cause their various ingredients to combine*, but when once formed, their *melting point* may be many degrees lower. Further, some silicates with low formation temperatures do not yield such fluid slags as others which may, nevertheless, require a higher combining temperature. Slags of the latter class though practicable are more costly, as they

need extra coke to superheat them to fluidity, but other economic factors often necessitate their use.

Continuing, the specific gravity of the slag must be low enough to permit the smaller globules of heavier matte to sink readily during "settling," whilst, finally, the flux must be as cheap as local circumstances permit. The latter consideration usually is the main factor, ideal metallurgical requirements having to give way to financial needs. A certain slag, for example, might be greatly improved by the addition of lime, but in a district where limestone is not readily procurable it will be necessary either to manage without it or to restrict its use to the lowest limit. Such slags, through lack of sufficient lime may carry away more copper than they normally should, but if the cost of the lime (delivered to the works) be greater than the value of the loss in copper which its employment would prevent, it is obviously better practice to discard it.

In smelting ores rich in bases the addition of silica will usually be necessary, and where possible this requirement will be met by the admixture of the proper ratio of a siliceous copper ore, or of acid ores containing gold and silver, which may be purchased and smelted profitably with the main supply. The addition of barren flux, though frequently unavoidable, should always be restricted as far as circumstances permit.

The union of the bases with the siliceous constituents to form slag results in the production of silicates, some of which are readily fusible and others practically infusible. Smelters define the various slag silicates by a terminology which indicates the relative proportions of base and acid present in each—or, more correctly, the proportion existing between the oxygen in the base and the oxygen in the silica. Thus, the silicate

represented by the general molecular formula " $\text{RO} + \text{SiO}_2$,"¹ is termed a "*bisilicate*," because the oxygen atoms in the acid (silica) are twice as many as are the oxygen atoms in the base.

Again, $2\text{RO} \cdot 3\text{SiO}_2$ would be a *trisilicate*, there being six atoms of oxygen in the acid to two in the base.

A silicate slag-type of great importance to the copper smelter is the *sesqui-silicate*, which has the general formula $4\text{RO} \cdot 3\text{SiO}_2$, containing six atoms of oxygen in the acid to four in the base, and may be regarded as a mixture of a singulo-silicate ($2\text{RO} \cdot \text{SiO}_2$) with a bisilicate. This is, perhaps, the best slag for most purposes, as it possesses several desirable properties from the smelter's point of view.

In ordinary works' practice, if the total oxygen in the slag approximates closely to 32% by weight, irrespective of the actual "oxygen-ratio," the smelter can usually be sure of a freely-flowing and generally good slag. Any variation from this oxygen percentage, as ascertained by slag analysis, can be corrected by the addition to the charge of a heavy or light base, or of acid (silica), according to their known oxygen contents, so as to bring the whole to the required 32% O.

The sesquisilicate of iron ($4\text{FeO} \cdot 3\text{SiO}_2$) contains 38.5% of silica and has a formation temperature of $1120^\circ\text{C}.$; ² but as a slag composed entirely of this silicate would have a relatively high specific gravity, tending to hinder the efficient settling out of the matte, it should preferably be lightened by replacing some part of the oxide of iron by a chemically equivalent

¹ In these formulae, the letter R represents one atom of a divalent element, such as Calcium, Barium, Magnesium, Ferrous Iron, or Manganese; or two atoms of a monovalent element, as Sodium; or two-thirds of the atom of a trivalent element, such as Aluminium.

² *Principles of Copper Smelting* (Peters); p. 375.

quantity of an earthy oxide, such as lime, so as to still maintain the desired "oxygen ratio"; or, to employ a synonymous term, the "silicate degree." In copper smelting the slags are practically limited in the upper range of silica proportions to the bisilicates, as those which contain a higher proportion of acid to base (such as trisilicates) are unworkable at the temperatures which obtain in the copper blast furnace.

An example of a bisilicate slag may be considered: assume a slag¹ to contain—

SiO ₂	=	45%
FeO	=	23%
CaO	=	24%
		92%

To ascertain its silicate degree, it is necessary to compare the ratio of the oxygen in the bases on the one side with that present in the silica on the other side; thus—
ON THE BASES SIDE—

<i>FeO</i>			
Atomic weight of Fe	=	56	
" " O	=	16	
Molecular " FeO	=	72	

Consequently, since 72 lb. of FeO contain 16 lb. of O,

$$23 \text{ lb. " " } \frac{23 \times 16}{72} = 5.1 \text{ lb. Oxygen.}$$

<i>CaO</i>			
Atomic weight of Ca	=	40	
" " O	=	16	
Molecular " CaO	=	56	

56 lb. of CaO containing 16 lb. of O,

$$24 \text{ lb. " will contain } \frac{24 \times 16}{56} = 6.86 \text{ lb. of Oxygen.}$$

$$\begin{aligned} \text{Total Oxygen in bases} &= 5.1 \text{ lb.} + 6.86 \text{ lb.} \\ &= 11.96 \text{ lb.} \end{aligned}$$

¹ This is a type of "high silica slag," such as has been produced at the Granby Smelter.

ON THE ACID SIDE—

SiO_2		
Atomic weight of Si	=	28
„ „ O	= 16(× 2)	= 32
Molecular „	SiO_2	60

60 lb. of SiO_2 containing 32 lb. of O,
 45 lb. „ will contain $\frac{45 \times 32}{60} = 24$ lb. of Oxygen.

Thus the atoms and percentage weight of the oxygen in the acid are practically double that contained in the bases, and the slag is, therefore, a bisilicate of the formula $RO.SiO_2$. It will be noticed that the above analysis adds up only to 92%; the balance will be alumina, magnesia, and small amounts of other ingredients whose acid and basic oxygen contents may be assumed approximately to balance, and thus not to affect materially the general character of the slag.

The foregoing calculation illustrates the methods of arriving at the silicate degree or oxygen ratio of a slag from its percentage composition. The next example shows the principle adopted in calculating the flux additions (if any) necessary to produce a slag of given silicate degree from an *ore* of known analysis. For the purpose of illustration an ore of basic character is selected.

ORE COMPOSITION

	%		
CHALCOPYRITE (Cu_2S Fe_2S_3)	25.42	{	Cu 8.79%
			Fe 7.75
			S 8.86
PYRITES (Fe S_2)	10.57	= {	Fe 4.93
			S 5.64
CALCIUM CARBONATE ($CaCO_3$)	47.14	= {	CaO 26.40
			CO_2 20.74
SILICA (SiO_2)	7.70	=	7.70
ALUMINA (Al_2O_3)	3.30	=	3.30
FERROUS OXIDE	0.19	=	Fe 0.15
FeO (combined as silicate)			O 0.04
Water and undetermined	5.68	=	5.68
	100.00%		99.98%

A "smelting analysis" of this ore would express the above contents in the following way—

Cu	=	8.8%
S	=	14.5%
CaO	=	26.4%
SiO ₂	=	7.7%
Al ₂ O ₃	=	3.3%
FeO	=	16.5%

the totality of the iron present being here calculated to ferrous oxide.

Considering the matte-forming constituents (copper, iron, and sulphur), about one-half of the sulphur will be volatilized in the upper zone of the furnace, leaving 7.25% which will enter the matte (see page 72).

As each 1 lb. of copper present requires 0.25 lb. of sulphur to form Cu₂S, 8.8 lb. will absorb 2.2 lb. of sulphur, and will leave a balance of, say, 5 lb. S. Every pound of sulphur left combines with 1.75 lb. of iron to form FeS, and 5 lb., therefore, requires 8.75 lb. of iron, which is equivalent to 11.25 lb. of FeO; leaving 5.25 lb. FeO to pass into the slag. Hence, the matte from 100 lb. of this ore must consist of—

Cu	=	8.80 lb.
Fe	=	8.75 lb.
S	=	7.25 lb.

24.80 lb.

and will contain 35.48% of copper.

The remaining slag-forming constituents per 100 lb. of ore are thus—

CaO	=	26.40 lb.
SiO ₂	=	7.70 lb.
Al ₂ O ₃	=	3.30 lb.
FeO	=	5.25 lb.

Assuming that it has been decided to form a sesquioxide slag, the lime (CaO) will be present as 4 CaO

3 SiO_2 , and $(56 \times 4) = 224$ parts of CaO will require $(60 \times 3) = 180$ parts of SiO_2 ; or 26.4 lb. of lime require 21.2 lb. of silica.

If the calculation be worked on the oxygen ratio, i.e. $1 : 1\frac{1}{2}$, then as CaO contains 28.6% of oxygen, sufficient silica must be supplied as will contain—

$$\frac{28.6 \times 26.4 \times 1.5}{100} = 11.325 \text{ lb. of O.}$$

Therefore the silica required will be—

$$\frac{11.325 \times 60}{32} = 21.2 \text{ lb.}$$

which agrees with the figure previously obtained.

Similarly alumina¹ contains 47% of oxygen, hence the oxygen requirements are—

$$\frac{47 \times 3.3 \times 1.5}{100} = 2.326 \text{ lb. of O.}$$

which will be satisfied by 4.36 lb. of SiO_2 .

Finally, FeO contains 22.22% of oxygen, and the oxygen requirements are—

$$\frac{22.22 \times 5.25 \times 1.5}{100} = 1.75 \text{ lb. of O.}$$

and is satisfied by 3.3 lb. of SiO_2 .

Thus the total silica required is—

For the CaO	=	21.20 lb.
„ Al_2O_3	=	4.36 lb.
„ FeO	=	3.30 lb.
		28.86 lb.

Of this amount, the ore already contains 7.7 lb., leaving 21.16 lb. to be added. It will be understood

¹ In this calculation the alumina is considered to act as a base.

that 21.16 lb. of *pure* silica are required, which must be supplied from the most suitable source of siliceous material at command. If such be found by analysis to contain, say, 90% of free silica, it does not follow that all of this will be available for fluxing, as some or all of the remaining 10% may be basic material, which, in turn, will require to be satisfied with some of the 90% of silica, thus leaving something less than 90% for fluxing the ore. In this event, it will be necessary to employ a proportionately larger amount of the impure silica in order to provide the 21.16 lb. of free, or *efficient*, SiO_2 required.

The resulting slag derived from ore and flux combined will be—

		per 100 lb. of ore smelted.	composition of slag.
		lb.	%
CaO	=	26.40	41.37
Al_2O_3	=	3.30	5.17
SiO_2	=	28.86	45.22
FeO	=	5.25	8.22
		63.81	99.98

Such slag, however, will have too high a "formation temperature" (see p. 62), being too rich in silica and lime; so, presuming it has been found impracticable to remove any of the lime by previous concentration, means must be adopted to improve still further its composition. The obvious way would be by addition of iron oxide, as iron-ore, or preferably, burnt pyrites, if the latter contains any copper. In the absence of copper the residual sulphur which this material usually contains would be objectionable. If it is desired to adhere to the sesquisilicate slag the proper amount of silica must also be added to flux this. As, however, the amount of silica added for this purpose would be less

than the oxide of iron addition (in the proportion of 0.625 to 1), the ultimate composition of the amended slag would be improved by a reduction of the percentages of silica and lime. The addition from external sources of the whole of the extra iron required would, however, be unnecessarily expensive, as there is, in part, an already available supply if that which enters the matte as FeS be reduced.

This may be accomplished by reducing the percentage of *sulphur* in several ways, for example—

1. Roasting the ore before smelting.
2. Increasing the volume of blast.
3. Increasing the size of the charges.
4. Reducing (if possible) the amount of coke.
5. Adding oxidized copper ores.

The first method reduces the amount of sulphur and alters the composition of the matte by enriching it with copper, whilst leaving iron for slag purposes. Methods 2, 3, and 4 may be employed separately or together, as each tends to produce an oxidizing atmosphere in the furnace. Such treatment would, therefore, not only render the slag more workable, but would also improve the value of the matte.¹

In the above example no note has been taken of dust losses, nor of the influence of the ash from the coke, which also forms slag.

Alumina is generally an objectionable material in slag formation, its action being uncertain. According to circumstances it may act either as an acid or a base, though in calculating the charge mixture for a desirable slag, it is safest at first to assume that it will behave as an acid, and to supply sufficient base to flux it, subsequently reducing the proportion of added base

¹ Strictly speaking, the last method does not eliminate sulphur, but "rescues" the iron from the matte.

by degrees until the best working limit is reached. The general effect of alumina is to thicken the slags and give them a sluggish flow.

Lime and oxide of iron have been mentioned as the more commonly used bases, but they may be replaced within certain limits by others; thus, iron oxide may be replaced by protoxide of manganese, and lime by baryta. Entire replacement in the latter instance is undesirable on account of the high specific gravity of baryta, whilst its high molecular weight gives it a very low replacement value, thereby unduly increasing the slag production and diminishing the capacity of the furnace. To a limited extent magnesia may, and in ores containing it must necessarily, be employed. This earthy oxide would, at first sight, appear ideal for fluxing silica owing to its low combining weight, only 40 parts being required to flux 60 of silica to bisilicate degree, as against 65 parts of lime; but, if present in any quantity magnesia causes a marked rise in the melting point of the slag, which rapidly becomes viscous and sticky. Zinc oxide is also undesirable as a base, though amounts of from 10% to 12% may be safely carried; this oxide also has the effect of thickening the slags.

Peters quotes a useful table from Balling's *Compendium der Metallurgischen Chemie*, for calculating slag compositions showing the parts by weight of bases required to flux one part of silica, and the parts by weight of silica required for one part of base, to form various silicates. This table is reproduced on page 72.

Matte. — Matte consists essentially of cuprous sulphide (Cu_2S) homogeneously mixed with varying proportions of ferrous sulphide (FeS), and with or without dissolved iron, or magnetite (Fe_3O_4). It may also carry some arsenic and antimony (as arsenides and

One part by weight of Silica requires :	Parts by weight of Bases.	One part by weight of Bases requires :	Parts by weight of Silica.
For SINGULOSILICATES		For SINGULOSILICATES	
Lime	1.86	Lime	0.535
Magnesia	1.33	Magnesia	0.750
Alumina	1.14	Alumina	0.873
Ferrous Oxide . .	2.40	Ferrous Oxide . .	0.416
Manganous Oxide.	2.36	Manganous Oxide.	0.422
For BISILICATES		For BISILICATES	
Lime	0.93	Lime	1.070
Magnesia	0.66	Magnesia	1.500
Alumina	0.57	Alumina	1.747
Ferrous Oxide . .	1.20	Ferrous Oxide . .	0.833
Manganous Oxide.	1.18	Manganous Oxide.	0.845
For SESQUISILICATES		For SESQUISILICATES	
Lime	1.24	Lime	0.803
Magnesia	0.88	Magnesia	1.125
Alumina	0.76	Alumina	1.310
Ferrous Oxide . .	1.60	Ferrous Oxide . .	0.625
Manganous Oxide.	1.57	Manganous Oxide.	0.633

antimonides), nickel, bismuth, etc. (if these elements are present in the ore) also any gold and silver carried by the charge. In many cases the primary object of matte-smelting may be the treatment of gold and silver bearing ores which contain but small amounts of copper. Sulphide of copper has the property of collecting the precious metals in marked degree, and it has been established that as little as 0.5% of copper in the charge is enough for this purpose, if a sufficiency of sulphide of iron be also present. For efficient collection the resulting matte should contain at least 8% of copper.

The amount and richness of the matte for a given ore content of copper will, therefore, depend primarily on the percentage of sulphur in the charge. Copper

having a greater affinity than any other metal for sulphur, in calculating the amount of matte producible from a given charge, the factors first to be determined are the percentages of copper sulphur and iron in the charge (see page 67); further, the amount of blast, depth of the charge, and other conditions will each have its bearing. The copper will first satisfy itself with sulphur to the extent required to form Cu_2S ; of the remaining sulphur, some will burn off, and the balance will combine with iron to form FeS . In this connection, it should be mentioned that iron pyrites (FeS_2) is dissociated at a comparatively low temperature into free sulphur, which distils as such, and into ferrous sulphide which remains; hence, roughly half the sulphur present in the charge as iron pyrites is lost in the upper zone of the furnace and does not enter into consideration as far as matte formation is concerned.

Where mattes are produced for subsequent treatment by "converting" (or "Bessemerizing") the copper content aimed at is about 45%. If it much exceeds this figure there will be insufficient iron and sulphur to supply the necessary heat, resulting from their oxidation, which is required in this further operation. Again, as the separation of matte from the slag is never quite complete, the richer the matte the greater will be the total copper lost in the form of finely divided suspensions.

On the other hand, too poor a matte means an unduly large quantity for converting and refining, a disadvantage which may necessitate its re-smelting with siliceous material in order to bring it up to a suitable richness. This practice is sometimes followed in "pyritic smelting" (*q.v.*) where large quantities of low grade matte are produced.

Flue Dust.—A considerable amount of dust is necessarily produced, not only from the blast furnaces but

also from the roasting furnaces and converters. The amount naturally varies with the proportion of fines in the charge and the strength of the blast, and will commonly be from 3% to 10% upon the total charge. The furnaces are therefore connected with dust-chambers and long flues, in which the velocity of the waste gases is so much reduced as to effect the deposition of all but the lightest particles. The flues are sometimes built above ground, in which case they are provided with hopper-bottoms from which the collected dust is periodically removed. This dust, which is frequently richer than the original charge (always much richer in the case of converter dust), as before mentioned, is usually dealt with either by returning it to the blast furnace, after roughly briquetting, or by smelting in a reverberatory furnace with "fine" concentrates. In some cases, it is mixed with the converter slags before returning to the furnace. When the briquetting method is adopted lime is generally employed as a binder to the extent of 4% to 5%.

Flue dust is a constant source of loss and trouble, and it can hardly be said that any really satisfactory method exists for its treatment.

Difficulties of settlement are still more serious in lead smelting, on account of the poisonous nature of the fine dusts, and many devices are in use to prevent their discharge into the air. Filtration of the waste gases, after preliminary settling in flues and dust chambers, is carried out in "bag-houses," the gases being led into and passed through the fabric of long bags suspended in a large chamber. The dust collects inside these and is recovered by periodically shaking them, and discharging the contents through a neck at their lower ends.

Another system employs a number of metal plates

or wires (a development of the latter being known as the Rösing system) suspended in the dust chamber with the object of providing an extended surface for condensation; it has been found that, independent of reduction in gas velocity, (which should not exceed 4 ft. per second in the last chamber) the greater the surface area with which the gases are brought into contact the better the deposition of solids. The "Cottrell" process provides a highly efficient method of dust settlement; it depends upon the passage of static or high-tension electric charges through the gases, which travel between a number of wire conductors in a specially designed chamber; the electric discharges cause the dust suspensions to precipitate, while much of the sulphur trioxide vapour is also deposited therewith.

At one works near Salt Lake City, where, owing to the fineness of the charge, a high percentage of dust was produced, a water spray was provided within the mantle walls of the blast furnace and effected considerable improvement. At Mansfeld, where combustible waste gases are produced (see page 61), these were, at the time of the author's visit, some years ago, being purified by water-washing in a "Theissen" centrifugal apparatus and dried by passage through a vapour separator.

Furnace gases after more or less complete deposition of their solids still contain sulphurous acid, which is discharged into the air from the main chimney-stack, except in a few works where it is collected and converted into sulphuric acid. The amount of sulphur lost in a large works is enormous, amounting to 400 or 500 tons per twenty-four hours in extreme cases.

CHAPTER VII

THE TREATMENT OF MATTE

Two systems may be employed in this succeeding operation, namely, "converting" or Bessemerizing, or treatment by roasting and further smelting in a reverberatory furnace. The former is adopted in most of the large works, but cannot be used efficiently for an output of less than 30 tons of copper per day.

Converting.—This operation, which consists in blowing air through the molten matte contained in a "converter," was patented in Great Britain by Hollway in 1878, followed closely by Manhés, who established it successfully at the Parrot Works, Butte, Montana. Until recent years, the blowing was universally performed in vessels lined with siliceous (or acid) material. Although this practice has been almost completely abandoned in favour of the "basic-lined" converter, a brief description of the older method will be of interest in showing the advantages of the more recent departure.

Converters are of various shapes and sizes, the following being a description of the old acid-lined converters of the "Calumet & Arizona" plant, at Douglas. They consist of a barrel-shaped steel shell in two sections, the upper portion being bolted and keyed to the lower, so that the two portions can readily be taken apart for re-lining. The shell is provided with riding rings which run upon rollers, whereon it can be turned by suitable gearing, for receiving the charge and for discharging the finished contents. The back of the converter is fitted with a longitudinal wind-box communicating with the tuyères through which the air is forced into the matte,

well below the surface. The upper section is furnished with a pyramidal shaped throat through which the spent air-blast is discharged. The turning mechanism is actuated either by hydraulic or electric power. These converters are 7 ft. in diameter by 10 ft. 6 in. long, and are lined with silica (or siliceous copper, gold, or silver ore) mixed with sufficient clay to bind the whole. In some instances the shell is first lined with chromite or magnesia bricks and the silica lining superimposed. The lining is roughly shaped round a central core, which is withdrawn after the plastic mass has been forced tightly into place by rammers operated by compressed air. The lining is about 2 ft. in thickness in the body, but gradually tapers off to a few inches at the throat. The tuyères are punched through with a steel bar when the lining is ready for drying. The lining is dried by making a wood and coke fire inside, though occasionally molten converter slag is poured into the converter (the tuyères being temporarily plugged with clay) and left for about an hour, when the still molten centre is poured away, leaving a frozen shell over the dried lining. A considerable saving of time is claimed for the latter method, the converter being ready for use in seven hours, in place of twenty-four hours required by fire-drying; nevertheless the latter is more usual practice. A steel converter shell 8 ft. by 11 ft. weighs about 10 tons, and carries 15 tons of lining.

The converter is now removed from the lining bed and placed upon the working stand, the air connections are made, and it is ready to receive its charge of molten matte. This is usually poured into it from a ladle, the converter having been tipped to bring the mouth into the necessary position, and at such an angle that the tuyères are clear of the matte. After receiving a

working charge it is turned back to the normal, the air blast having previously been turned on.

The effect of blowing air through the matte is that the iron sulphide is first oxidized to ferrous oxide (which combines with the silica of the lining to form ferrous silicate slag) and to sulphur dioxide; but part of the sulphur in the matte still remains combined with the copper at this stage. Continuing the blow the latter sulphur gradually oxidizes, finally leaving metallic copper, which is cast direct into moulds from the tipped converter. From its appearance the metal so produced is called "blister copper"; it contains about 99% Cu, with some dissolved oxide of copper and sulphur dioxide gas. Air blast at a pressure of 8 to 12 or even 16 lb. per square inch is employed.

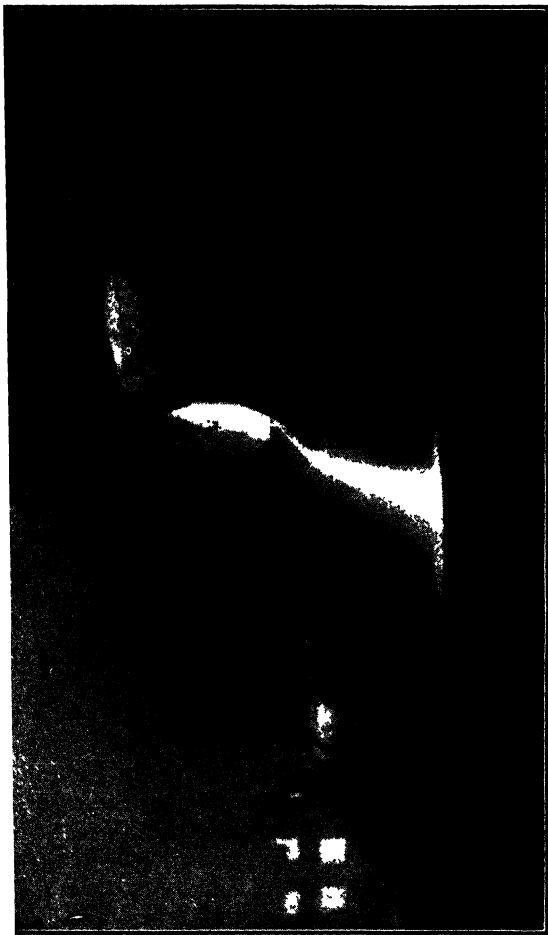
After the iron has been oxidized and has formed slag at the expense of the lining, the converter is tipped and the slag poured off, leaving cuprous sulphide, or "white metal"; the converter is then again turned back to the working position and the blow continued till the residual sulphur is fully oxidized, and only copper remains. Considerable practice and skill is required in working, the operator judging of the changing condition of the converter contents by the colour and nature of the flame issuing from the mouth, or more usually, by the appearance of the metal which adheres to the "punching rod" when introduced through the tuyères. This is especially the case in basic converting (*q.v.*), and the approach to the "finish" can also be observed when prills of copper issuing from the mouth adhere to the converter hood.

An acid-lined converter 8 ft. by 11 ft. will deal with 10 to 12 tons of 50% copper matte at each "blow," and will produce about 15 tons of blister copper before re-lining becomes necessary. When the lining is so

far corroded as to necessitate renewal the shell is lifted from its stand and transferred to the lining-bed, a freshly lined shell taking its place: the former is cooled with water and re-lined without delay. Converter slags, being rich in copper, are returned to the blast furnace for re-smelting, and form part of its normal charge.

The expenses and labour involved by "converting" in *acid* linings were long recognized by all smelters, and efforts were made to overcome, at least partially, the constant re-lining operations by charging siliceous ores into the converter with the matte, in order to save the silica of the lining; but little effective advance resulted in this direction. At first, the general experience of skilled smelters as to the prospect of converting in *basic* lined converters did not appear encouraging; nevertheless, by constant experimenting, the various difficulties were gradually overcome and success attained, until nowadays it may be said that practically every acid-lined converter in the United States has been thrown out in favour of the basic-lined. Many have contributed to this improvement, but the names of Baggaley and Heywood stand out as pioneers of the later process; whilst to Smith and Pierce also is due much of the credit for developing and bringing it to its present state of wide application. It would appear that many of the earlier failures were due to the use of converters too small in size, and with increasing capacities the employment of the basic lining became more and more practicable. Herman A. Keller says:¹ "The recent successes with basic converter linings are the direct outcome of the larger vessels which are necessitated by the newer plants to handle larger quantities."

¹ *Trans. Amer. Inst. Mining Eng.* Vol. XLVI, p. 475.



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20-FT. GREAT FALLS CONVERTER AT ANACONDA

Two forms are in common use: the "Granby" or upright, and the "Smith-Pierce" or barrel-shaped converter. Theoretically a basic lining should never be destroyed in a properly run converter, but wear, particularly in the region of the tuyères, takes place, especially if the temperature is allowed to get too high. In practice the actual basic-brick lining is protected by an artificially produced layer of magnetite, derived from low-grade matte by blowing without the addition of any siliceous material. Great heat is developed, which is then checked by the further addition of cold matte, resulting in the formation of magnetite (ferro-ferric oxide); this substance, in the absence of acid (siliceous) material, remains unaltered. The magnetite forms a coating on the brick work, and thereafter becomes the true lining, which can be increased or decreased in thickness at the will of the operator. To Wheeler and Krejci is due the credit of this discovery, which they patented in 1913.¹ Other workers, however, claim to have made use of this system, though perhaps without fully recognizing the importance of the part played by magnetite; leaving aside the question of priority it is sufficient to state that this system, when skilfully applied, renders the lining of a converter practically permanent.

The latest practice is to form a further skin of alumina upon the magnetite lining, by the addition of this material, in one form or other, to the matte prior to the introduction of siliceous material. The reason for this is that magnetite (especially when treating mattes containing Fe_3O_4) is prone to accumulate, and being infusible gradually reduces the capacity of the converter; the skin of alumina prevents these growths.

At the first "blow" of a new converter the metal

¹ U.S. Patent 14,068,70

tuyère pipes burn back into the lining for a distance of about 2 in., this deficit being maintained as the lining wears away; when therefore re-lining becomes necessary the tuyère pipes must also be renewed.

Each time that a basic-lined converter cools down—from causes such as shortage of matte or power stoppage—the drop in temperature causes the flaking off of 2 or 3 in. of the surface. It is most important, therefore, to ensure that a sufficiency of fresh matte is at hand, and that an independent gas fuel supply be laid on to maintain the proper temperature in case of need.

When it is realized that with the older acid process a fresh lining was required after every three or four blows, the importance of the indefinitely prolonged basic lining will be appreciated. The whole of the re-lining department can now be dispensed with, whilst the number of shells for a given output is reduced to a minimum, there being no need for idle units other than one in reserve in case of accident.

The siliceous material (which must be thoroughly dry and in pieces below $1\frac{1}{2}$ in. in diameter) is added to the charge through the mouth of the converter in the proportion necessary to flux the iron oxide; the difference between the two methods being that in the acid process the iron is removed at the expense of the lining, whilst in the basic process the silica is supplied as part of the charge. The air-pressure employed is similar in both cases.

“The trend in converting is towards the use of the Pierce-Smith basic converter, now standardized to a size of 13 by 30 ft.”¹

¹ *Mineral Industry*, Vol. XXXIV, p. 251.

CHAPTER VIII

SMELTING IN THE REVERBERATORY FURNACES

THE reverberatory furnace was in use in South Wales for copper smelting long before blast-furnace practice developed in America, all the operations in the old Welsh practice, from matte smelting to metal refining, being conducted therein. But it again fell to American metallurgists to develop this branch of the art to its present efficiency. The Welsh reverberatories were constructed with oval hearths about 14 ft. long and 8 to 9 ft. in width at the widest part, having a capacity of from 5 to 10 tons per day. The modern American furnace hearths reach 116 ft. in length and 19 ft. in width; while those erected by E. P. Mathewson at Anaconda have a capacity of no less than 300 tons per day, and one has treated 402.5 tons of charge in twenty-four hours for a consumption of 1 ton of fuel per 6.45 tons of charge.¹ In recent years even these dimensions have been exceeded, but the present tendency is towards some reduction in these extreme lengths.

In reverberatory smelting the reactions are brought about simply by the addition of heat to the charge, no complications being introduced by the presence of carbon and oxygen as in the blast furnace. It is simply a melting-down process applied to a suitably prepared charge. Very little oxidation of the charge material by air takes place, as the firebox is kept full of fuel and the working doors and all openings for charging are kept closed, as far as possible, to prevent loss of heat. In this respect also the operation differs from

¹ Mathewson; 8th Internatl. Congress of Applied Chem., 1912.

reverberatory roasting where the object is to admit air to oxidize the sulphides.

The furnaces, being required to resist a high temperature, are solidly built structures. At Anaconda, their side-walls, of silica brick, are from 2 to 3 ft. thick, and the roof (of the same material) 15 in. thick, which will last about twelve months. The hearths are of highly siliceous sandstone, 2 ft. thick, "burnt-in" in one firing. The whole furnace is built upon a solid block of slag cast from another furnace; this provides a better foundation than concrete. No tie-rods pass under the furnace, as the buck-staves are sunk 2 ft. in the ground against a solid block of slag. At the works of the Canadian Copper Mining Co., at Copper Cliff, where copper-nickel ores are worked, magnesite¹ bottoms and linings are employed. Brick-hearths have been used but burnt-in silica bottoms are now more common.

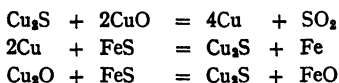
The silica may be burnt-in in one or two stages, and is finally coated with slag and low-grade matte melted in to fill any cracks or interstices. At one time much care and labour, with several firings, was expended in making the hearth, but latterly the process has been simplified to the above. The prior treatment with low-grade matte prevents the absorption of rich matte which would otherwise take place when smelting commences, although the latter is occasionally used.

The furnace charge consists of calcined (or roasted) ore and concentrates, sufficient sulphur being left in the "calcines" to satisfy matte-forming requirements. Where possible the hot ore is delivered from the roasting furnace direct, in order to prevent chilling, and the necessary flux (usually a little limestone only) is sometimes added to the ore in the roasting furnace, whereby

¹ Calcined carbonate of magnesia.

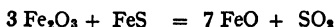
good mixing is ensured and the benefit of the preliminary heating extended to the flux also.

The production of the matte depends upon a number of more or less complex reactions between oxide and sulphide of copper, and copper and sulphide of iron, as to which the following are typical—



The ferrous oxide shown to be produced in the last equation then combines with the silica present in the ore to form the required silicate of iron slag.

During the prior calcination of the ore much of the iron has been oxidized to the ferric state (Fe_2O_3), which must be reduced to ferrous oxide (FeO) before it can combine with the silica ; this reduction is brought about mainly by the ferrous sulphide (FeS), thus—



In reverberatory smelting, as in the blast furnace, the success of the operations depends primarily upon the affinity of the copper for sulphur, any of its oxidized compounds being converted to sulphide at the expense of other sulphur compounds present. It is for this reason that the copper is prevented in so marked a degree from forming silicates and thus becoming part of the slag. Nevertheless some silicate of copper is invariably formed, and precaution is often taken to reduce its amount by distributing a layer of pyritic material over the slag ; this in sinking through effects a reduction of the oxidized copper, and further tends to sweep down any suspended particles of matte.

Reverberatory slags are generally more siliceous than those of blast furnaces ; indeed it is important to keep

them strongly acid in order to prevent the base constituents of the ore from attacking the siliceous furnace side lining. The hearth itself is protected from such action by the layer of matte. Typical slags contain from 40% to 45% silica, 25% to 30% iron, 5% to 10% lime, and 0.3% to 0.4% copper. In Swansea practice still more siliceous slags were produced, carrying over 50% silica; but some of this is in the form of free suspended fragments which are withdrawn with the slag during skimming.

With coal as fuel a long-flamed bituminous variety is used, as it is necessary to maintain a strong heat over the extensive hearth; the ratio of hearth area to grate area in large modern furnaces is about 16 to 1, and the fuel consumption, in average cases, from 20 to 30 tons per 100 tons of ore smelted. In earlier practice large charges of 10 tons or more were made through hoppers placed above the arch of the furnace and near to the bridge end, but it is now customary to feed smaller charges at more frequent intervals, whereby greater uniformity in furnace temperature is ensured.

When the charge is smelted the slag is "skimmed," or run out, through the skimming door into slag cars and sent to the dump—the term "skimming" surviving from older practice where the slag, being too siliceous to flow freely, was drawn from the surface of the matte by a rabble. The slag if too thin was deliberately thickened by cooling, as there is more danger of removing matte with slag if both be equally thin. In present practice the larger slag quantities are allowed to flow from the furnace, as distinguished from a true skimming operation, and in some cases they are granulated in a stream of water and washed down a launder to the waste heap or into cars for removal. The matte-tap is then

opened and the matte drawn either into ladles for conveyance to the converters, or cast into cakes if not required for immediate conversion.

The furnace acts as a convenient store for matte, only such quantities as are required for converting being drawn therefrom. In fact it is not usual to tap the furnace "dry," as the layer of matte forms an excellent protection for the silica bottom and serves to supply and distribute the heat to fresh ore-charges. Repairs to the lining are required from time to time, particularly at the "wind-and-water" line near the hot end of the furnace and along the bridge wall, the operation being termed "fettling." Formerly repairs were effected by tamping-in a mixture of clay and siliceous material after more or less completely emptying the furnace; but the present practice is to add powdered siliceous ore through small openings in the roof along the side of the furnace: where a weak spot has developed a convenient hole is opened and the added material allowed to fall into position, when it is pressed into place. In this manner, the wear at the "slag-line" is kept in constant check.

At several of the smelters in America and Mexico oil-fuel has been substituted for coal; the ordinary firebox and bridge is dispensed with, the oil being fed through the back wall by pipes, and sprayed into the furnace by steam or compressed air. A very hot flame is thus obtained which is capable of easy regulation, the system possessing several advantages over coal-firing. Remarkable results have been achieved, and one obtained by Sörensen at Steptoe, McGill, in 1911, in which no less than 666 tons of charge were smelted in twenty-four hours, may be quoted¹—

¹ E. P. Mathewson; 8th Internatl. Congress of Applied Chem., New York, 1912.

Total charge per furnace-day.	666	tons
Oil fired per furnace-day	421	barrels
Coal-equivalent for oil used	124.0	tons
Total charge per barrel of oil	1.58	tons
Oil, barrel, per ton of total charge . . .	0.63	
Equivalent (gross) coal per cent of total charge	18.60	

The following was the resultant slag analysis—

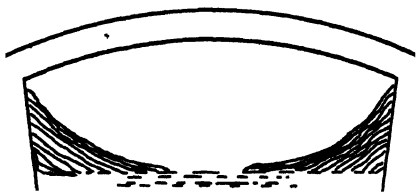
		%
Cu	=	0.4
SiO ₂	=	44.0
FeO	=	34.3
CaO	=	8.6
Al ₂ O ₃	=	7.4
Oxygen ratio	=	2.72

The matte contained 40.4 % copper

In modern reverberatory practice coal-dust is frequently used for firing the furnace, the coal being dried, crushed to fine powder (approximately, 100 mesh), and injected by air-pressure into the furnace. The advantages established are: (1) less fuel consumption per ton of charge smelted; (2) increased size of furnace; and (3) more rapid smelting, with consequent increase of charge smelted per unit area of hearth. S. S. Sørensen is credited with the first successful application of coal-dust firing to copper smelting at the Highland Boy Smelter, near Salt Lake City. Some trouble was at first experienced in regard to the coal-ash, which tended to form a heat-insulating layer above the charge; the dust also deposited in the flues and fouled the tubes of the boilers which are set in them at the end of the furnace for the purpose of utilizing the waste heat. The former objection is not serious, as the dust, being mainly siliceous, is fluxed by the basic slag; whilst the latter has been largely overcome by avoiding bends and sharp turns in the flues, thus permitting a passage free from obstructions to the gases. David H. Browne

refers to the application of this system at the works of the Canadian Copper Co.,¹ and in the same issue is a record of its utilization at the Washoe Reduction Works by Louis V. Bender. At the latter, the fuel-ratio (tons smelted to fuel used)—including drier coal—is given as 7.08 : 1.

In more recently constructed furnaces, arrangements are made for charging the ore to be smelted along the



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CROSS-SECTION OF REVERBERATORY FURNACE
(Showing banking of charge)

entire length of the hearth, a practice which almost completely obviates fettling.²

A fourth method of firing is by means of producer gas with or without a heat regenerative system. An example of this is supplied by the regenerative furnaces at Kyshtim, Siberia, designed by W. G. Perkins, which have given good results technically and economically.

In large modern plants for matte smelting the reverberatory has almost entirely superseded the blast furnace, though the latter may, as previously mentioned,

¹ *Bulletin (Amer. Inst. Min. Eng.)*; Jan., 1915.

² Owing to litigation over the Carson patents for side charging, there has lately (1927) been a tendency to revert to the practice of dropping the main charge near the firing end of the furnace.

find renewed application for the smelting of sintered material.

Mention has been made of the utilization of the waste heat from reverberatory furnaces by installing boilers between the flue and the stack. In the older coal-fired system considerable power was thus developed, and the same economy is practised in the latest coal-dust installations, although in these the spent gases leave the furnace at a lower temperature. This however is no disadvantage, as obviously the first duty of a furnace is to smelt ore, and if this could be accomplished without loss of heat ideal fuel efficiency would be reached ; but as this is manifestly impossible of realization, such heat as passes from the furnace in the waste gas is best utilized for steam raising purposes. Louis V. Bender (*op. cit.*) states that attached to one of the 124 ft. $\times$ 21 ft. Washoe reverberatories are two batteries of " Stirling " boilers, each of which develops 650 h.p.

CHAPTER IX

THE WELSH PROCESS SMELTING FOR "BLACK COPPER"

THE origin of copper smelting in Great Britain is obscure, but it seems probable that rude blast furnaces were used long before the reverberatory was adopted. For an account of the early metallurgy of copper the reader is referred to Percy's standard work on Metallurgy.¹ In view of present-day conditions it is interesting to quote the first sentence of his preface, written from the Government School of Mines, London, November, 1861; he says: "In no country are the operations of metallurgy conducted on so vast a scale as in Great Britain." Unfortunately this statement is no longer true, for though (particularly in the production of iron and steel) we are able to hold our own as far as quality goes, we have long lost the first position with regard to quantity. It is unlikely that Percy could have foreseen the gigantic scale on which smelting operations are now being conducted; the treatment at a single works of 15,000 to 20,000 tons of copper ore per twenty-four hours (as in America) would have been regarded as the sheerest improbability at the time he wrote. In those days South Wales was an important centre for copper production and received rich ores from all parts of the world; but as the sources of ore developed in importance local smelters were gradually installed to treat the ore on the spot—a course generally more profitable than freighting them to Wales. Before that

¹ Percy's *Metallurgy*. London, 1861.

time there was but little competition ; consequently " returning charges " for smelting the ores ruled very high—to the temporary benefit of the Welsh smelters.

The opening up of the low-grade " porphyry " deposits of Western America has, perhaps, had a preponderant effect in placing the United States at the head of the world's copper producers ; it was realized that the profitable treatment of these poor ores could only be possible by operating on a very large scale involving heavy capital outlay and financial risk. Moreover, it must be recognized that their conditions were and are by no means favourable as to locality, i.e. in relation to the supply of fuel and raw materials generally. They also had, and have, to reckon with a higher cost of labour than in Europe.

One reason for the advance of the smelter's art in America is the free interchange of knowledge, experience, and ideas between metallurgists, to the exclusion of the cult of " secret processes." On this point, we cannot do better than quote the words of Dr. L. D. Ricketts :¹ " I believe . . . for the advancement of our art we should deliberately discuss subjects among ourselves, in order to do away with the idiosyncrasies of the individual and to gain a composite view representing the best thoughts of many men." This is the mature view of one of the first authorities on copper metallurgy, and who, though he would be the last to admit it, has more to give than to receive ; it would be to our advantage if similar views found wider acceptance in our own land.

The Welsh Process, from which modern reverberatory smelting has sprung, was originally carried out in six separate operations.

¹ *Bulletin (A.I.M.E.)* ; Apr., 1915 ; p. 711.

1. *The Calcination of the Ore*, or preliminary roasting in a reverberatory furnace; this removes the greater part of the sulphur, leaving sufficient only to produce in the next, or matteing operation, a matte or regulus carrying about 30% copper, known as "coarse metal." Calcination is a simple oxidizing roast of the ore and calls for no special comment.

2. *Melting to Produce Coarse Metal*.—This also is carried out in a reverberatory, but higher temperature is employed and air is excluded, the furnace in consequence having a larger grate area in proportion to the hearth or "laboratory" part. As in America, the working-bottom is of silica, usually burnt-in in two layers; the upper and thinner one is the true or "working" bottom, which can be replaced from time to time as it becomes destroyed, whilst the lower one lasts a longer time but eventually has also to be renewed. The old bottoms become saturated with regulus, and when removed are re-smelted for their copper contents. The furnace is provided with a skimming door for slag removal, whilst the coarse metal is tapped out through a hole provided for the purpose. The charge generally consists of a mixture of partially calcined ore with a proportion of "raw" ore containing sulphides and oxidized minerals, which mutually react, forming matte and slag with evolution of sulphurous acid gas. It is not usual to tap the matte at each charge; after "skimming," a fresh ore charge is introduced and smelting re-started, a portion of the matte being drawn after the smelting of the second charge has proceeded sufficiently, leaving enough behind to cover the furnace bottom in order to protect it and distribute the heat.

Slags from the "fine-metal" furnace (a later operation) are usually included as part of the coarse-metal charge, as they contain too much copper to be discarded.

A charge weighs about $2\frac{1}{2}$ tons, four of these being smelted per twenty-four hours. The slag which results ("ore-furnace slag") is clean enough to be thrown away. The regulus or matte, granulated by flowing in a thin stream into a pit filled with water close to the furnace, is collected, drained, and sent forward to the next operation.

3. *Coarse Metal Calcination*.—The granulated coarse metal is calcined in a furnace similar to that used for roasting the raw ore, the object being to oxidize the sulphide of iron constituent of the matte, leaving most of the copper still as sulphide. The iron so oxidized is slagged off in the following or smelting process.

4. *Melting the Calcined Coarse Metal*.—This is performed in a melting reverberatory of the type employed for coarse metal; the "calcines" are mixed with siliceous ores, old silica-bottoms, and rich slags from the refinery furnaces, the whole charge being made up with sufficient silica to flux the oxide of iron produced by the previous operation (3). The products from this furnace are "white metal" and "metal slag," the latter being re-smelted in operation (2). "White metal" should contain 70% to 73% of copper; if lower in grade, it is termed "blue metal"; and if richer (75% to 80%), "pimple metal," from its peculiar appearance on cooling. This is due to the evolution of sulphurous acid during setting which produces a rough, irregular surface, whilst the interior shows cavities containing threads or filaments of metallic copper.

5. *Roasting*.—In Welsh practice this term is restricted to the oxidation and smelting of white metal to "blister" copper, the earlier desulphurizing processes being termed "calcining." The white metal, in large lumps, is charged irregularly into the furnace in such a

manner as to leave air-channels between them. A high temperature is required, sufficient air to promote oxidation being led into the furnace through the bridge, which is hollowed for the purpose. The air is thus heated before it enters the hearth, whilst at the same time by cooling the bridge it reduces the wear on the latter. The action of the heated air on the white metal produces cuprous oxide, with evolution of sulphur dioxide, the cuprous oxide in turn reacting with any unaltered sulphide of copper, yielding metallic copper and further sulphur dioxide; this action continues until the white metal is wholly converted to metallic copper. A certain amount of slag is produced from the action of the oxides of iron and copper on the silica of the furnace, as well as upon silica adhering to the regulus from the sand moulds in which it is cast; such "roaster-slag" is re-treated in operation (4). The metal carries about 95% of copper, and is known as "blister" from the appearance given to it by the evolution of sulphur dioxide during setting.

6. *Refining*.—Blister copper contains iron, sulphur, arsenic, etc., as impurities, which to a large extent are removed by refining. To this end the copper is again melted upon a reverberatory hearth which slopes in all directions to a well placed near the end door; air is now admitted and the copper stirred to assist oxidation, chiefly of the iron. Not only are the impurities oxidized, but sub-oxide of copper is simultaneously formed which dissolves in the copper to a certain degree of saturation. Seven per cent of cuprous oxide is usually aimed for, the product being "dry" copper—the operator judging by the fracture of a test-piece when this condition is reached. The slag is now "skimmed" and the surface of the metal covered with charcoal or anthracite. The next step is the reduction of the dissolved cuprous

oxide and the production of "tough pitch" copper by introducing a pole of green wood under the surface of the molten metal. Vigorous ebullition results from the gases evolved by the wood, and from the bringing of the molten metal into contact with the reducing layer of charcoal; sulphur dioxide is also liberated during the operation. It is important that the dissolved cuprous oxide shall not be completely reduced, as a small amount (up to 1%) improves the quality of the metal and confers toughness.

During the process samples are taken from time to time, and from their appearance the condition of the metal and the progress of the operation are judged. "Under-poled" metal shows a depression when the ingot sets; as the proportion of oxide falls the depression lessens until a flat surface results, at which stage the copper is "tough pitch," and is ready for ladling into moulds. This condition must be maintained during casting by the introduction of air, or further reduction, as may be necessary. The presence of residual cuprous oxide ensures that any other impurities shall be present only as oxides, and further it prevents the copper from dissolving gases. "Over-poled" copper, on the other hand, sets with a longitudinal ridge and must be "burnt" or "flapped" back to "dry" copper, and then re-poled.

Smelting for Black Copper

In the preceding pages, the methods of production of copper from sulphide ores has been outlined, but, before leaving this branch of the subject, mention must be made of the smelting treatment of oxidized ores for the production of *black copper*, though the supply of metal from this source is relatively small.

Black copper is an impure metal, containing iron

and other impurities which require to be eliminated by refining. As oxide of copper readily unites with silica, when smelting oxidized minerals it is necessary to prevent this combination by maintaining a strongly reducing atmosphere in the blast furnace, a condition necessarily resulting in the reduction of some of the iron oxide to metallic iron which alloys with the copper.

It is further essential to maintain a high temperature in order to ensure the copper remaining molten in the crucible, and the slag must possess great fluidity to allow of complete settlement of metallic prills. Subject to the above limitations, the general procedure is similar to that of matte-smelting, though with some differences in manipulation and plant arrangement ; thus no settler is used, the metal being allowed to accumulate in the crucible whence it is tapped intermittently into moulds. A brick-lined spout is used for the reason that water-jacketing would chill the metal. The crucible is preferably of brick, sometimes with no "bosh," and should rest on the ground instead of being carried upon jacks or other supports, in order to retain as much heat as possible. Should it be necessary to use an existing water-jacket furnace, the sole-plate should be dropped to the lowest possible position, where a brick crucible may be built upon it, any space beneath the plate being filled in with sand or similar non-conductor to prevent loss of heat by radiation.

If possible a little sulphide mineral should be used in the charge, as this will form a thin layer of regulus above the metal and assist in preventing the formation of copper silicate. The whole of the metal is not drawn when tapping, a layer of protecting regulus being left in the furnace. The slag is tapped as usual at a higher point, also intermittently, and if not clean enough, may be discharged into a settler.

Black copper is refined by re-smelting in a reverberatory furnace with sufficient flux to combine with the iron oxide produced; the slag should not be too fluid, but of such consistency that it can be drawn or pulled. When the charge is molten the furnace doors are opened to admit air, and the metal is "flapped" vigorously until all the iron is oxidized and removed as slag; this operation is performed by a long hoe-shaped rabble, suspended by a chain about the middle of the shaft, by means of which the metal is splashed about and fresh surfaces continuously exposed to oxidation. The heat is maintained by throwing logs of wood upon the molten metal, the ebullition of gases also assisting the oxidation. Flapping is continued until all the iron is oxidized, together with some copper, part of which forms silicate (refinery slags contain 9% and upwards of copper), but a considerable proportion remains dissolved as cuprous oxide. When this amounts to about 7% (as judged by the fracture of a test-piece), the doors are closed, and, after raising the heat, the metal is "poled" to pitch.

If the copper contains precious metals it is not brought up to pitch, but is cast into anodes for electrorefining. The cathode copper produced by this operation (depleted of its gold and silver) is usually re-smelted, flapped back to 7% Cu_2O , then poled up to pitch and marketed as "tough-electro."

CHAPTER X

ELECTROLYTIC REFINING

THE final process through which a large proportion of the copper of commerce passes is that of electrolytic refining. In the previous operations which end with furnace-refining, gold, silver, and small amounts of base metals are still retained in the copper, and the twofold objects of this further step are firstly, the recovery of the precious metals in saleable form, and secondly, the removal of the base impurities which adversely affect the conductivity of the metal required for electrical purposes.

The process consists in making an anode of the copper to be refined in an electrolyte of copper sulphate solution suitably acidified, a cathode of pure sheet-copper being provided to receive the new metallic deposit. On passing an electrical current through this system, the copper is continuously dissolved from the anode and re-deposited in pure form upon the cathode sheet; whilst the gold, silver, and other impurities remain undissolved under these conditions, and fall to the bottom of the electrolyzing tank as a mud, which is removed from time to time and treated for the recovery of its values.

The metal to be refined is cast into anode plates which are either provided with cast lugs for convenience of suspension in the electrolyzing tanks, or furnished with clips attached to the top edge.

The metal is cast either from the refining furnace or directly from the converter; the plate dimensions vary and may reach a size of 3 ft. square, with a thickness of

from 2 to 3 in., the measurement at Great Falls being 3 ft. by 2 ft., and $2\frac{1}{2}$ in. thick. The electrolyzing tanks are constructed of wood, lead-lined, of such cross-section as will conveniently accommodate the anodes, and of length to suit the requisite number of plates to be refined; twenty or more anodes, spaced about 5 in. between centres, with the same number of cathodes

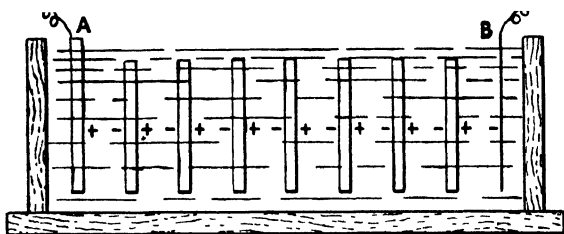


FIG. 1

DIAGRAM OF ELECTROLYTIC TANK (SERIES SYSTEM)

form a convenient unit, though in one case thirty pairs per tank are employed, anodes and cathodes being placed alternately in the tank.

Two systems of electrode arrangement are used, known respectively as the "series" and the "multiple," the latter being generally considered the more satisfactory. In the former a number of copper anodes are suspended uniformly in the tank without the use of separate cathode sheets, except as to the last plate on the negative side. The generator supplying the current is connected to the first and last plates only, as shown in the diagram. (Fig. 1.)

As the current enters and passes from the plate A, the metal is dissolved therefrom and deposited on the near side of the next plate, whilst the remote side of

this second plate acts as an anode from which the metal dissolves, again depositing on the near, or negative, side of the following plate ; and so on throughout the whole series until B is reached, which acts as a simple cathode. The copper deposited on the negative faces is stripped off, the negative surface having been

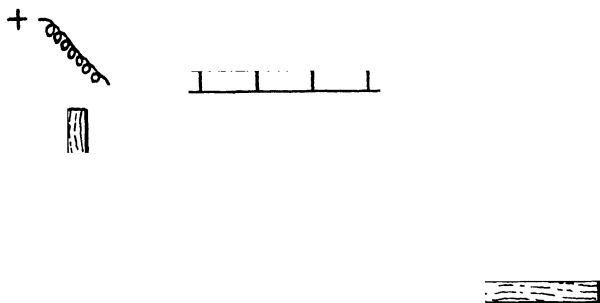


FIG. 2

DIAGRAM OF ELECTROLYTIC TANK (MULTIPLE SYSTEM)

dressed with a suitable conductor such as graphite, which prevents permanent adhesion. Theoretically each anode plate should be converted entirely to pure metal, but in practice irregularities in copper dissolution and re-deposition interfere with perfect working, some undissolved copper frequently remaining attached to the pure copper deposit from which it must be stripped for re-melting into fresh anodes. The chief advantages of this system reside in the small number of electrical connections necessitated, and in permitting the whole of the intermediate plates to be covered with the electrolyte, which results in less metal being left in the shape of "waste ends" for re-melting ; the preparation of a large number of cathode sheets is also avoided, but lead-lined tanks cannot be employed.

In the "multiple" system, the anodes and cathodes are arranged alternately in the tank, all the former being electrically connected in parallel with the positive pole, and all the latter with the negative pole. (Fig. 2.)

The cathodes or "starting sheets" are made by electro-depositing thin sheets of copper upon rolled-copper cathodes in a set of tanks apart from the general refinery; the rolled plates are dressed with oil and graphite to prevent close adhesion of the deposited sheet, which is stripped off when of sufficient thickness. At Great Falls the electrolyte used in the preparation of the cathodes contains 120 grms. of free sulphuric acid per litre and 40 grms. of copper in solution:¹ this differs slightly from the main liquor used in refining, which carries 153 grms. free acid and 41.1 grms. of copper per litre.

The current density varies from 15 to 20 amperes per square foot in most of the plants in the vicinity of New York, though this amount is sometimes exceeded. At Great Falls up to 35 amperes are used, with an efficiency of about 90%, and an average drop per tank of 0.6 volts; the anodes being soluble the electromotive force required is much less than would be the case were insoluble anodes employed. A certain number of tanks must be provided to recover the copper from the working solution which gradually enriches as refining proceeds; for this purpose insoluble anodes must be used, the tanks so engaged consuming about eight times the electrical energy of the ordinary refining tank.²

To assist the operation and to ensure uniformity of deposit, the electrolyte is kept in constant circulation,

¹ Willis T. Burns. *Trans. A.I.M.E.* Vol. XLVI, p. 716.

² W. L. Spalding. *Trans. Amer. Electrochem. Soc.* Vol. XVI, p. 127.

either by pumps or by arranging the tanks in cascade formation; the electrolyte is also heated to a temperature of about 130° F. (54° C.).¹ The average output of refined copper may be taken at 6 lb. per kilowatt hour. American refineries vary in capacity from 1,800 to 16,000 metric tons of refined copper monthly.¹

The production of new refined copper in the United States during 1926 is given as 2,358,532,017 lb., or 1,179,266 short tons, apart from 134,519,125 lb. imported.²

The following are the analyses of the anodes, of the electrolyte, and of the resulting products of refinery at Great Falls. (Burns.)

The silver and gold in the anode, calculated to troy ounces, show the following contents per ton—

Silver	=	39.99	ozs.
Gold	=	0.233	„

In the refined wire-bar metal from the re-melted cathodes the corresponding figures are—

Silver	=	0.875	ozs.
Gold	=		trace

and in the slime (mud)—

Silver	=	5012.87	ozs.
Gold	=	35.0	„

The cathode copper is re-melted in a refining furnace and finally brought up to pitch in the usual manner.

¹ L. Addick. *Trans. Amer. Electrochem Soc.* Vol. XXV, p. 69.

² *Min. Industry*, Vol. XXXV, p. 161.

CHAPTER XI

TREATMENT OF COPPER ORES BY WET PROCESSES

COMPARED with smelting the amount of copper produced by hydro-metallurgical methods is very small, though the importance of the latter is rapidly increasing. One reason for the restricted use of wet methods is that most copper deposits of importance carry certain amounts of silver and gold, which are recoverable by smelting with practical entirety at but small additional cost ; indeed there are cases where the presence even of a small quantity of precious metal may be sufficient to determine the commercial success of a copper-smelting proposition. On the other hand, wet processes, as at present developed, generally fail to recover the silver or gold, owing to the insolubility of these metals in the solution used to extract the copper ; where other conditions are equal, it is therefore, better practice to smelt these. Naturally this disadvantage does not apply to complex ores which contain valuable constituents in such amounts as render the copper of lesser importance. Thus an ore which carries high silver or gold values, with but a small quantity of copper and sulphur may be particularly suited to wet treatment, the copper being recovered only as an incidental step in a method devised mainly for silver or gold. Such in fact would be more correctly regarded as a silver ore containing copper rather than a copper ore carrying silver. In such cases local conditions will largely determine whether the treatment scheme should be based on methods more particularly adapted to silver ores, or treated from the first as a copper ore, with the

incidental recovery of silver,—there being no obvious dividing line either in the nomenclature or the treatment of ores containing more than one valuable constituent. The raw material most suitable for treatment by wet processes is that in which the greater part of the copper is present in an oxidized form, such as copper oxide, or carbonate; copper silicate, although an oxidized compound, is not so generally amenable to solvents. Means have, however, been devised for its effective treatment as will be mentioned later.

The ore must not contain undue amounts of other constituents soluble in the solutions employed. Thus where sulphuric acid is the solvent, carbonates of lime and magnesia must be absent or present only to a small extent, as these minerals would cause heavy consumption of the acid, possibly sufficient to render the cost of the operation prohibitive. Similarly alumina must not be present in large amounts. Here again circumstances will govern procedure, as unless very fine grinding be necessary to liberate or expose the copper mineral to the action of the solvent, the lime present may not absorb the full quatum of acid to complete sulphatization; each fragment will become coated with a protective layer of calcium sulphate, when further action ceases, and the balance of the acid will be available to dissolve the oxidized copper mineral. Further, the circumstances must involve reasonable cost of the solvent chemicals; whilst finally, precious metals should be absent if a simple process for the recovery of copper is to be adopted.

It is but rarely that all these conditions are found in one deposit, for though an ore may hold most of its copper as carbonate, it may yet carry sufficient sulphide mineral (which is not so suitable for wet treatment) to show a poor total recovery, in spite of a complete

extraction of the carbonate. Sulphides are, of course, convertible to oxides by calcining, but this would involve further cost. Wet processes have however been successfully applied to sulphide ore tailings, though the commercial importance of these operations is at present comparatively small, except at Rio Tinto, Spain, where unique conditions prevail. Even here, however, wet treatment is not practised so extensively as formerly, the adoption of pyritic smelting, combined with a ready market for the cupiferous pyrites rich in sulphur, having adversely influenced the earlier methods.

The Rio Tinto deposits are of massive pyrites containing about 3% of copper. The ore is built into heaps of a million tons or more, arranged with suitable ventilating flues and chimneys, and is sprayed with water to promote atmospheric oxidation of the pyrites. Ferrous sulphate is first formed, which slowly oxidizes to ferric sulphate and reacts with the cuprous sulphide to form soluble copper sulphate and insoluble cupric sulphide. The latter is again oxidized to cupric sulphate by the ferric sulphate and atmospheric oxygen. The treatment of such a heap takes about four years to complete. The solution draining therefrom contains both ferric and cupric sulphates, the former of which is reduced to ferrous sulphate by passage through a layer of fresh ore. This avoids unnecessary consumption of the pig-iron by which the copper from the cupric sulphate is replaced and precipitated. It will be evident that in this slow progressive chain of reactions the oxidation of the pyrites under working conditions is substantially limited to that necessary for the dissolution of the copper contents, since the ferric sulphate formed is again decomposed by the cupric and cuprous sulphides present in the mass. When these have been effectively dissolved the operation is finished. The sulphur content of the

pyrites itself does not materially diminish because the iron salt formed acts, cyclically, as a carrier of oxygen to the copper sulphides. The decrease in ore-weight is less than 7% and is therefore not much greater than that of the copper minerals dissolved.

The pigs of iron are laid in long troughs or trenches through which the solution is caused to flow slowly until completely depleted of its copper, the equivalent of iron being dissolved as ferrous sulphate. The precipitation of copper upon iron is known as "cementation," and the product as "cement" copper, or in Spain, "cascara." The cement copper is removed from the pigs from time to time, any undissolved iron being returned to the trenches until completely consumed. The product is a brownish-red powder consisting of metallic copper contaminated with more or less iron, graphite, etc., derived from the crude pig, and is smelted and refined in the usual way; 1.3 tons of pig-iron are consumed in depositing 1 ton of copper.

In many smaller installations scrap-iron is used for cementation in place of "pig"; recently, spongy-iron (reduced from calcined pyrites by heating with carbon) has been successfully used as a precipitant, and where calcines are available it promises to replace other forms; its preparation however demands some skill.

The chief acid solvents used in wet treatment are sulphuric and sulphurous acids for oxidized ores, and ferric salts—generally ferric sulphate—for ores containing sulphides. Many variations have been proposed, some of which have met with a measure of success. Thus the addition of "bleaching powder" to the sulphuric acid yields chlorine which converts any silver present into silver chloride; this may now be extracted by leaching with hyposulphite of soda. This method also dissolves gold which is recoverable by suitable means.

A preliminary roasting may often be advantageous even though the ore contains but little sulphur, the treatment dehydrating any associated clay and rendering the ore more easily percolable by the solvent. If moreover the ore contains some (or all) of the copper as sulphide, careful calcining will convert much of this into sulphate soluble in water; this effects a considerable saving in acid, as only such copper as remains in oxide or silicate form will require the solvent, any carbonate initially present being converted to oxide by calcination. In practically all cases the consumption of solvent is greater than that demanded by the copper alone, as other ore constituents containing iron, lime, alumina, zinc, etc., are also soluble to some extent in the acid. The amount of such acid-consuming substances present will determine whether the wet process can be economically applied or not.

Ores which contain a substantial proportion of sulphur may be roasted for the production of the sulphurous or sulphuric acid required in the subsequent treatment of their calcines; muffle-roasting furnaces are employed for the purpose in which the fuel gases from the grate are prevented from mixing with the sulphur dioxide derived from the ore. Usually, the fuel gases are caused to pass under the working hearth, returning above the arch. The latter in turn may be caused to heat the floor of a second working hearth superposed. Several hearths may be arranged in this manner, the ore being passed through them serially. The gases, rich in sulphur dioxide (6% to 7% by volume) and undiluted with fuel products, are led by flues to sulphuric acid chambers. An acid plant is, however, costly and is provided only in large installations.

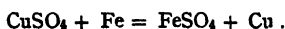
The simplest form of wet treatment consists in charging the suitably crushed ore into large vats fitted

with false bottoms through which a weak acid—usually sulphuric—is percolated until the copper is dissolved; and the resulting copper sulphate solution is precipitated by passage over scrap or pig-iron. The reactions involved (apart from many secondary effects) are—

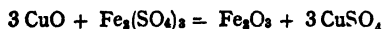
1. Solution—



2. Precipitation—

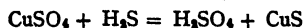


whence it is apparent that all the sulphuric acid is finally consumed in forming ferrous sulphate, a substance useless as a solvent. Many methods have been proposed to regenerate the solvent, the cost of which is a serious limitation. One of these is the oxidation of the ferrous to ferric sulphate, which now becomes an efficient solvent for cupric oxide—



Oxidation of ferrous sulphate is, however, a difficult matter, especially in the absence of free acid, as insoluble basic salts form which result in loss of acid radical; and it may be said that no application of this often proposed method has met with continued success.

If sulphuretted hydrogen gas be used to precipitate copper from its sulphate liquors the acid is regenerated, the copper being recovered as sulphide—



But the preparation of sulphuretted hydrogen on a large scale presents difficulties which have prevented its general adoption for the purpose. In the Laist process it is derived from calcium sulphide (obtained by heating gypsum with carbon) which on treatment with carbonic acid and water yields calcium carbonate and sulphuretted hydrogen.

A third method of precipitation with regeneration of the acid, is the electrolysis of copper sulphate liquors in cells furnished with insoluble anodes and cathodes of thin copper plate. The copper is deposited on the latter and the acid liberated at the surface of the former. The H_2SO_4 accumulates in the impoverished copper solution, which when sufficiently poor in metal to render further electrolysis uneconomical, is returned to extract a fresh ore charge. This would appear to be a simple operation but for the facts that suitable anodes are difficult to obtain, and that the working solutions are usually contaminated with other soluble matter derived from the ore. Whilst the latter drawback can be overcome by chemical means the anode trouble remains. For electrolyzing sulphate solutions peroxide of lead or antimonial lead anodes are partially satisfactory, but in presence of chlorine are rapidly decomposed. Anodes of lead containing 3.5% of antimony are reported to have given satisfactory results at New Cornelia Copper Co., Ajo, Arizona, but here the ore contains no chlorine.¹ For the less commercially important chloride solutions, when free from sulphates, graphite is the most suitable anode material. Fused magnetite anodes were at one time successfully used at Chuquicamata, but these have been replaced by duriron, a silicon-iron alloy.

From the point of view of capacity and output the most important example of hydro-metallurgical practice is that of Chuquicamata, Chile. This mine is probably the largest known copper deposit in the world, the amount of ore already "proved" being in the neighbourhood of 400,000,000 tons, averaging about 1.6% copper. Its chief copper mineral is an oxy-sulphate known as Brochantite, which though insoluble in water

¹ *Non-ferrous Metallurgy*. Liddell. Vol. II, p. 1081.

is readily dissolved by weak sulphuric acid. A certain amount of sodium chloride is found in the upper layers of the deposit, as also some Atacamite, or oxy-chloride of copper. The character of the ore at once suggested the adoption of a wet extraction method, which was ultimately developed from extensive preliminary tests. The present plant has a capacity when in full operation of about 12,000,000 tons of ore per year ; in 1926 over 8,000,000 tons were mined. The recovery of copper is about 87·5 per cent and the total cost rather less than 9 cents per lb. of copper produced.

The ore is mined by steam-shovel, and after crushing to about $\frac{1}{4}$ in. mesh, is delivered by belt-conveyors to the leaching tanks. These are of novel construction, being built of reinforced concrete, lined with a mixture of quartz and specially prepared asphalt ; filter-bottoms of wood and cocoa-matting are provided. The tanks are 16 ft. in depth, 160 ft. in length, and 110 ft. in width ; each is capable of taking a charge of 10,000 tons of ore, which is leached with weak sulphuric acid derived from the electrolytic precipitation plant. The presence of chlorides in the ore causes the formation of soluble cupric chloride, which if electrolyzed would necessitate the collection and utilization or removal of the chlorine gas simultaneously liberated at the anodes,—a difficult and complex operation to carry out upon so large a scale. In place of this, the chlorine was at one time removed by reducing the soluble cupric chloride to insoluble cuprous chloride by shot-copper, the solution being agitated therewith in passage through a revolving barrel. The attrition so afforded keeps the copper shot bright and constantly exposes fresh active surfaces to the attack of the solution ; the cuprous chloride suspended in the issuing liquor is readily collected in filter-presses and, after drying, is

smelted with coke and limestone to metallic copper. In more recent practice cement copper produced at the works has replaced shot copper. The sulphate solution now freed from chloride is sent to the electrolyzing plant in which the copper is deposited and sulphuric acid regenerated. As the ore contains the bulk of its copper as sulphate, it yields upon electrolysis sulphuric acid in excess of requirements, the supply of the latter being therefore in no need of additions from outside sources. In this respect Chuquicamata ore has a great advantage over others which contain their copper as carbonate or oxide.

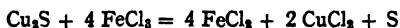
It is not economically possible completely to exhaust the liquors of their copper contents by electrolysis; according to Cappelen Smith¹ the solution sent to the electro-deposition plant contains approximately 5% of copper with $2\frac{1}{2}\%$ to 3% of free sulphuric acid, and after leaving it will still carry 1.5% of copper and 8% to 9% of free acid, which is returned for utilization on a fresh ore charge. Some idea of the size of this installation may be gathered from the statement that the electrolytic refining plant will have an output of 335,000 lb. (or $167\frac{1}{2}$ short tons) of copper per day; and when in full operation the production of metal is estimated to reach 60,000 tons per year, a figure which must later on exercise an important bearing upon the annual copper production of the world.

In this instance electrolytic precipitation is rendered easy by the relative purity of the solutions, particularly with regard to the absence of notable quantities of iron. If this be present in substantial amount (as would result from the acid treatment of roasted pyritic ore), its previous removal by some chemical precipitation method would be necessary, or at least desirable. A further

¹ *Trans. Amer. Electrochemical Soc.* Vol. XXV, p. 201.

difficulty in electrolyzing impure solutions is the non-uniformity of the copper (cathode) deposit. Some improvement may be effected by employing diaphragms, but few really satisfactory materials are available for this purpose. Nevertheless, porous bags—such as of canvas or glass-wool—have been used with considerable success (when made to enclose the anode tightly) at Karkaralinsk (Siberia), Trollhättan (Sweden), and Vienna.

Other wet treatment processes are based on dissolving the copper as chloride, either by the direct use of hydrochloric acid, or by means of ferric or ferrous chloride. Chloride solutions are in some respects easier to deal with than those of sulphates, in being amenable not only to precipitation methods suitable for the latter, but also to other methods. Local conditions seldom permit of the use of hydrochloric acid, as it is difficult to transport in bulk and consequently costly. Ferric chloride though also costly, has the advantage of dissolving not only oxidized minerals but cuprous sulphide (Cu_2S) also—



The ferrous chloride formed may be re-oxidized in part by aëration or electrolysis, and thus regenerated for further use. Again the copper may first be obtained as a sulphate solution and converted to chloride by the addition of salt. Chloride processes are useful where the ores contain silver, the silver chloride being extracted by dissolving in brine or a strong solution of other metallic chlorides. The copper may be precipitated by iron, as in the case of sulphates, or it may be treated with sulphurous acid gas whereby under low pressure cuprous chloride, and at higher pressure metallic copper, are formed.¹ Cuprous chloride may be reduced by

¹ L. D. Ricketts, *Trans. Amer. Electrochemical Soc.* Vol. XXXVII, p. 41.

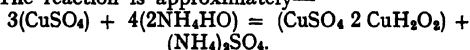
metallic iron, or smelted with lime and carbon to copper.

Lime has many times been suggested as a suitable precipitant for copper chloride solutions, as the calcium chloride produced is soluble. On the other hand, it cannot be employed with copper sulphate solutions, as insoluble calcium sulphate would be precipitated with the copper hydrate and heavily contaminate it.

Neither do the reactions involved result in clean copper hydrate, the precipitates being invariably accompanied by basic salts derived from the precipitant. Thus when calcium chloride is used to decompose copper sulphate, the calcium sulphate deposit always contains basic salts of copper. Similarly when lime is employed for the precipitation of copper chloride solution the hydrated copper oxide carries in addition copper oxychloride, and often lime salts. It is probable this incompleteness of separation is responsible for the fact that none of these processes so often proposed, have yet eventuated in large scale success.

It has been suggested that ammonia may be used to precipitate copper sulphate liquors resulting from an acid leach; the ammonia gas (regenerated from the ammonia-recovery plant) being passed as produced directly into the copper liquors, which should be kept well agitated. Under these conditions a granular precipitate of hydrated-oxide of copper with basic copper sulphate,¹ is obtained in a form readily capable of filtration and washing; this, when dried and calcined, is reduced to metal in the usual manner. The clear filtrate contains the ammonia originally added, but in the form of sulphate. When heated with an equivalent

¹ The reaction is approximately—



of slaked lime, in the usual ammonia-recovery plant, NH_3 gas is liberated, available for a fresh charge of copper liquor, and so on ; thus—



If the proper conditions be observed practically no ammonia is retained by the copper precipitate, whilst the cost of its regeneration is very low if modern stills of the type used for the recovery of ammonia from shale-products be adopted. The ammonia in this way acts as an intermediary between lime and sulphate of copper, the lime finally carrying away the sulphate radical without the possibility of contamination of the copper hydrate with calcium sulphate.

In recent years the recovery of copper from oxidized ores by leaching with ammonia has assumed considerable importance. Copper carbonate is soluble in a solution of ammonia and ammonium carbonate, forming a deep blue solution of cuprammonium carbonate from which the metal is recovered as oxide by boiling with steam at a pressure of about 30 lb., the ammonium carbonate being volatilized and recovered for re-employment as an aqueous condensate. The practically pure oxide is dried and smelted to metallic copper.

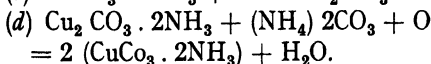
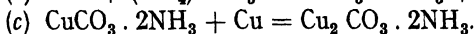
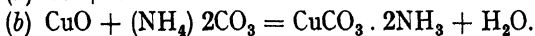
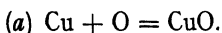
This process has been developed by the Kennecott Copper Corporation in Alaska for dealing with the copper carbonate minerals present in the ore-product after removal of the sulphides (chalcopyrite, covellite and some bornite) by water concentration. The presence of substantial amounts of calcite and dolomite in these residues precludes the use of acid solvents.

The leaching operation is conducted in large tanks fitted with filter bottoms. The "fresh" solution contains 5 to 6% of ammonia ; after some hours of quiescent contact with the ore-charge percolation is started and

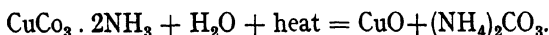
continued till the extraction of the oxidized copper is commercially complete. After filtering off the copper-bearing solution the drained ore charge is steamed for some hours; this provides effective washing and recovers by volatilization any remaining ammonia. The total ammonia loss is rather under 1 lb. per ton of the sands treated.

A similar use of ammonia is made in dissolving native (metallic) copper at the Calumet and Hecla Mines. Here 2,000 tons of low-grade sands are treated daily, with a recovery of about 75% of their copper contents at a cost of about 6 cents per lb. of copper recovered. The copper being in the metallic form oxygen in addition to ammonia is required to effect solution. This is furnished by the cuprammonium carbonate solution formed in course of the operation, which acts as a carrier of atmospheric oxygen to the copper to be dissolved. Thus the cuprammonium carbonate attacks and dissolves native copper, forming the corresponding cuprous salt; this readily absorbs atmospheric oxygen and reproduces the active solvent, and so on. These recurring reactions may be represented by the equations—

Dissolution—



Distillation—



The Calumet and Hecla tanks hold 1,000 tons of sands; the cycle of leaching operations occupies about 90 hours.

The employment of ammonia has recently found further application to oxidized ores containing copper silicates, (chrysocolla, etc.) minerals which are unattacked by the ammoniacal solutions previously dissolved. The frequent occurrence of chrysocolla in oxidized and siliceous ores, therefore presents a problem with which such methods could not deal.

The Perkins process overcomes the difficulty by subjecting silicated ores to a short preliminary heat treatment in an atmosphere of reducing gas, the temperature employed being about 400°–450° C. Under these conditions the copper silicate is reduced, the resulting product in which the copper disseminations are extremely fine, being now readily soluble in cuprammonium solvent. The reduction of the silicate is continuously effected in revolving cylinders; the issuing product, after cooling in the reducing atmosphere is leached with the solvent and the copper oxide recovered as before described.

This process is now being worked on a large scale at the Bwana M'Kubwa Mine in Northern Rhodesia, where a plant of over 1,000 tons per day has been installed. Despite tropical conditions the extensive ammoniacal leaching and distillation circuits are handled with a loss of ammonia no greater than at Kennecott in Alaska. The small loss is replaced by ammonia from a Mond gas plant which has been installed to operate with the local fuel from the Wankie coal-field.

The copper oxide produce is smelted to copper of exceptional purity, which is marketed under its own brand.

The development of the wet metallurgy of copper cannot be dealt with here in greater detail, but the subject is receiving much attention, and considerable advance will doubtless be made in the near future.

Numerous low-grade deposits of oxidized copper exist which will not bear the cost of smelting methods, and the only prospect of converting them into valuable sources of copper appears to be in the adaptation of a suitable leaching method. From data already established the cost of wet treatment of oxidized ore, where available, and under what may be called average conditions, should not exceed 4d. per lb. of copper produced, upon a plant capacity of not less than 100 tons per day. According to W. L. Austin,¹ "a siliceous² oxidized copper ore carrying 1.5 to 2 per cent metal may be profitably leached under favourable conditions."

For low-grade sulphide ores the problem is more difficult, but present indications are that the flotation method will gradually extend its application to ores of even greater leanness than those which it so successfully treats at present.

¹ *Trans. Amer. Inst. M.E.* Vol. XLIX, p. 667.

² Refers to the constitution of the gangue and not to silicate of copper as the mineral to be leached.

CHAPTER XII

COSTS AND MARKETING

SPACE does not permit of any close analysis of the costs of the various operations required in the production of copper, as conditions (character of ore, cost of raw materials, labour, fuel, distance from market, etc.) differ greatly with locality; so much so, that working expenses in one place may greatly exceed those in another, but under the particular circumstances the higher figure may nevertheless indicate the better practice. The "output" or works capacity also has a necessary bearing on the cost of metal produced. Heath Steele¹ has estimated the cost per lb. of copper produced in the United States, showing it to amount on the average to 10 cents,² or, in round figures, £41 per short ton of 2,000 lb.; but, as he points out, the price to the consumer is considerably greater, because to the cost of production must be added the profit made by all intermediaries through whose hands the metal passes; and, further, the stock issued for promotion, or in payment of the property, requires its legitimate share of the profits. To meet these and all other claims he estimates that 40% to 50% must be added to the production cost to arrive at the price paid by the consumer.

In the United States, which from its large production

¹ *Eng. and Mining Journal*. 9th Aug., 1913; p. 251.

² Recent reports in individual cases show costs as low as 7 cents.

leads the copper market of the world, four classes of metal are listed—

1. "Lake."
2. "Electrolytic."
3. "Pig."
4. "Casting."

"Lake Copper" is the produce of mines of the Great Lake district, and was at one time considered to be superior to metal derived from any other source. Since the introduction of electrolytic refining, however, the product so obtained has fully equalled "Lake"; indeed, at the present time the great bulk of copper produced in the States is "electrolytic," and, unless otherwise specified, the price quoted refers to this material. "Pig Copper" is the metal produced from the converters after furnace refining, and is sometimes pure enough for sale as "Casting" copper; it is largely exported. "Pig" which contains sufficient silver or gold to pay for electrolytic refining is always subjected to electrolysis. "Casting Copper" is the metal in ingot form cast in moulds furnished with partial wedge-shaped partitions which nearly divide the ingots into two (or more) parts, to facilitate their breaking for charging into crucibles for brass-making, etc. Other forms in which copper is sold are cakes for rolling into sheets, and "wire-bars" of rectangular section for drawing into wires.

Most of the copper made in the States is sold through one or other well-known agency, though some of the large producers market their own metal. Formerly the sales were effected on a cash basis, but latterly it has been the custom to allow thirty days after delivery to the manufacturer or user, the price quoted including cost of delivery to the buyers' works. For export business the price quoted is c.i.f. (cost, insurance, and

freight) to some European port. For details as to the handling and selling of copper in the States, the reader is referred to articles by W. R. Ingalls,¹ to whom the author makes acknowledgment for the information given above.

In Great Britain, the practice adopted in the sale of ores and metal is as follows—

During the past fifty years the method of marketing copper ores has undergone many changes; the old system of sending ore to smelters for treatment at fixed prices gave place to selling by "ticketing," which was a style of auction sale. This in turn was superseded by private treaty between buyer and seller, a method which long retained many of the ancient customs, such as "21 cwts. to the ton," a "draftage" allowance, variations according to price of coal, etc. Of late years, however, these practices have become obsolete, the bargaining between buyer and seller being shorn of such imposts and reduced to a simplified concrete custom.

A mine having produced a quantity of ore, it is offered direct to one or other of the copper smelting companies, or placed for sale in the hands of some recognized firm of metal brokers, who undertake the transaction on an arranged scale of commission. The ore is delivered by the mine, c.i.f. (usually at some British port), and the transaction resolves itself mainly into the agreement between buyer and seller of the "Returning Charge" (or smelting expense), which will vary according to the richness of the ore; the lower the produce, or copper yield, the higher will be the returning charge. The returning charge having been agreed, the copper contents of the ore are paid for, less the returning charge. This may be specified either "per

¹ Ingalls, *Eng. and Mining Journal*, Vol. XCIII, pp. 887, 939.

ton of fine copper," or "per unit," but in either case the result is the same; the term "unit" being, as the word implies, one-hundredth part of 1 ton, or 1%. Thus, "2s. per unit" would be 2s. $\times$ 100, or £10 per ton of fine copper.

It is apparent that some "basis" price is necessary upon which to fix the value of the metal contents; for this purpose it is customary to take the average of the official prices of "Best Selected Copper," ("B/S")—as quoted on the London Metal Exchange—for a short period before and after the arrival of the ore at the port of delivery; usually fifteen days before and seven days after. The practice of averaging prices over a period is an advantage both to buyer and seller in avoiding the market fluctuations of any particular day. If one day only governed the price this might be the occasion of a sharp though temporary rise or fall in market price, whereas a longer period ensures a fairer current market value.

The method of arriving at a "basic price" being agreed, and the returning charge fixed, the "Settled Dry Assay" of the ore is finally required. The "wet" weight of the parcel (i.e. that of the ore as received) is taken, the percentage of moisture (ascertained by sampling and assay) deducted, and the "dry weight" arrived at; this, at the agreed copper assay gives "fine" copper contents. Agreed official B/S, less the agreed R/C, gives the price *per ton* of "fine" copper contained. If the price per ton *of ore* is desired, then $B/S \div 100 = \text{price per unit}$; from which deduct R/C (on the unit basis) and multiply by the assay.

Other details may govern the transaction. Thus, the "B/S" basic price may be "net," or subject to discount, etc. It is usual for the sellers to appoint some firm of assayers to look after their interests, whose experienced

representative attends the works of the smelter on the arrival of the ore, superintends the weighing of the parcel and its sampling, and forwards an accurate sealed sample to his principals for assay, on behalf of the seller. Upon an appointed day the buyer and seller exchange the results of their respective analyses and agree as to a "settled" assay. Usually, it is stipulated in the ore-contract that assays are to be made by the electrolytic method, and 1.3 units deducted to arrive at the "dry" assay on which payment is made.¹

The *bona fides* of the seller being beyond question, payment is in many cases arranged as to 80% of the approximate value on or against the delivery of the ore, the balance becoming due on "settlement of assays," etc.

In most cases it is arranged that the purchase is for copper ore said to contain about —% Cu, and the R/C basis is fixed accordingly. Should the settled assay turn out below the contract figure, an increased R/C would be demanded by the buyer; it is therefore necessary that the assay of the bulk-ore shall be an accepted figure, arrived at by exchange of assay figures, according to definite trade custom. It is also understood that the copper ore offered for sale shall be of good quality and contain no deleterious elements—if such be present the buyers will reject the parcel, or exact a penalty for the impurity.

An alternative method for disposing of ore is for the seller to consign the parcel to one of the copper smelting

¹ The "dry" or smelting assay is presumed to indicate more nearly the amount of copper recoverable by smelting methods. In earlier days the "dry" assay method was used exclusively, and upon the results payment was made *without* deduction. Since the introduction of the wet method of assay, which shows the true copper content, the deduction of 1.3 units is assumed to correspond with the amount of irrecoverable copper. This does not apply to low-grade ores in the United States, which are subject to special terms.

firms, who on arrival will receive and assay the parcel, and render an Account Sales at best possible value, the latter being arrived at by the custom mentioned. This method, however, is rarely used, as it is obviously better for terms to be agreed previously, and for the sellers to be represented at the sampling and assaying operations.

It will be apparent that the returning charge is the amount which the smelter receives to enable the ore to be treated, or its contents brought into a marketable form of refined copper (which may be "Best Selected Ingots," "Tough Ingots," or "Tough Cake") and to pay his profit on the operation. Having brought the copper into one or other of these descriptions, a market is found through selling agents, and the copper is sold to customers, the price of the ingot or cake being governed solely by conditions of supply and demand. The smelter must take upon himself the onus of the rise or fall of the market between the time the ore is received and that at which a sale of the finished product is made.

Ingots and cakes are known as "unmanufactured copper," whilst metal treated by rolling and turned out as sheet, rod, plate, etc., is termed "manufactured."

The price charged for these varieties will of necessity vary with the amount of work involved in their manipulation (e.g. sheets may be very thin or thick, whilst rods vary to any desired diameter), it is therefore evident that a common basis is also necessary for the sale of manufactured copper. This was fixed early in the history of the British copper trade by the manufacturers applying the term "Strong Copper" to certain sizes and substances, and arranging a list of "extra" prices to be surcharged on descriptions of metal outside these limits. A basis price is fixed for "Strong Copper,"

which varies according to the price of Raw Copper, whilst the extra charges remain the same, or alter only when rendered necessary by increased cost of labour, etc. The price of "Strong Copper" is therefore constantly moving, whilst that of the Extras is rarely altered. A user of copper sheets, rods, or plates, will ascertain the price of any size or substance of article by taking that quoted per ton for Strong Copper and adding thereto the extras from an "Extra List," issued by copper manufacturers to their customers. Similarly with Brazed or Seamless Copper Tubes, certain sizes are adopted to form a "basis" selling price, with extras for other sizes "as per list."

Quite apart from the general methods of buying and selling just described, stands the production and marketing of "Standard" copper. This term is applied to certain brands of rough metal of 97% Cu, and to Refined Ingots which are registered on the London Metal Exchange after certain regulations have been fulfilled. When a lot of 25 tons or more of one of these brands is produced, the metal is placed in a registered warehouse, the weight and assay being certified by independent parties. A "Warrant" is then issued, bearing a full description of the parcel, and this certificate of existence of the copper passes freely between buyers and sellers until such time as it is purchased by a buyer desiring to take delivery of the metal; when, on presentation of the Warrant at the warehouse, the parcel is delivered. Standard copper, therefore, represents a stock of metal of known quality, actually in existence and stored at defined warehouses, whereof the holder of the warrant is for the time being the owner.

The foregoing is a brief general description of the methods by which copper is bought and sold, though many variations subsist in detail.

APPENDIX

REPRODUCED by permission from Quin's *Metal Handbook and Statistics*, 1928.

BEST SELECTED COPPER AVERAGE PRICE PER TON (excluding fractions of one penny)

	1923	1924	1925	1926	1927
Jan.	£ 69 s. 2 d.	£ 66 s. 13 d.	£ 70 s. 6 d.	£ 63 s. 16 d.	£ 61 s. 11 d.
Feb.	72 6 3	67 5 10	68 15 7	64 - -	60 7 6
Mar.	77 7 9	70 18 9	66 14 8	62 10 3	61 13 1
April	77 13 1	69 1 4	64 3 1	61 1 4	60 10 3
May	71 12 9	66 11 11	63 8 7	60 14 4	59 12 6
June	70 16 8	65 15 7	63 1 11	62 4 2	58 7 6
July	69 2 9	65 13 7	64 - 10	64 - 10	58 15 3
Aug.	67 13 4	67 4 8	66 3 1	66 - 10	60 18 7
Sept.	67 3 9	66 15 10	65 14 2	65 9 4	60 11 11
Oct.	64 8 4	66 17 -	65 1 11	65 4 8	61 18 9
Nov.	65 14 2	68 1 10	65 10 -	64 7 6	63 8 7
Dec.	66 10 4	69 14 4	64 7 -	63 8 7	65 9 2
	69 19 3	67 11 3	65 12 4	63 11 7	61 2 1

STANDARD COPPER AVERAGE CASH (and three months' for 1927) PRICES, PER TON (excluding fractions of one penny)

	1923	1924	1925	1926	1927	3 Months
Jan.	£ 64 s. 11 d.	£ 61 s. 6 d.	£ 66 s. 2 d.	£ 59 s. 1 d.	£ 55 s. 9 d.	£ 56 s. 3 d.
Feb.	67 15 3	63 3 7	64 15 6	59 14 7	54 10 1	55 1 1
Mar.	73 18 4	66 3 11	62 19 1	58 13 3	55 19 11	56 10 10
April	73 4 8	64 8 -	60 12 9	57 5 2	55 2 1	55 13 8
May	67 10 6	62 1 4	60 3 10	56 11 1	54 11 10	55 3 6
June	66 13 5	61 8 6	59 19 2	56 16 9	54 1 3	54 13 9
July	65 6 10	61 14 3	61 10 7	57 18 6	54 11 8	54 19 9
Aug.	64 1 8	63 10 10	62 13 6	58 18 4	55 8 -	55 15 3
Sept.	63 5 1	62 16 3	61 18 11	58 15 4	54 9 9	54 19 -
Oct.	60 13 6	62 14 -	62 - 9	58 7 3	55 3 -	55 5 3
Nov.	61 14 2	63 15 10	61 6 10	57 7 1	58 17 3	58 18 -
Dec.	62 1 11	65 6 10	59 12 -	56 18 7	60 2 3	60 5 7
	65 9 9	63 4 2	61 19 8	58 - 9	55 13 10	56 2 5

Reproduced by permission from *Quin's Metal Handbook and Statistics*, 1928.

COPPER—CASH PRICES
STANDARD COPPER (LONDON), PER TON

	Highest			Lowest		
	£	s.	d.	£	s.	d.
1908 .	65	2	6	56	2	6
1909 .	64	3	9	54	10	—
1910 .	62	1	3	52	15	—
1911 .	64	—	—	53	7	6
1912 .	80	1	3	60	17	6
1913 .	77	2	6	61	15	—
1914 .	66	15	—	51	15	—
1915 .	86	12	6	57	7	6
1916 .	153	5	—	85	2	6
1917 .	140	5	—	110	5	—
1918 .	120	—	—	110	5	—
1919 .	117	10	—	73	10	—
1920 .	122	5	—	70	—	—
1921 .	75	5	—	65	5	—
1922 .	66	2	6	57	—	—
1923 .	76	12	6	59	2	6
1924 .	68	15	—	60	7	6
1925 .	67	18	9	59	1	3
1926 .	60	11	3	56	3	9
1927 .	60	18	1	52	18	9

The following figures reproduced by permission from *Quin's Metal Handbook*, show the comparative average prices (omitting fractions of a penny) of the different grades of the metal for the year 1927.

Settle- ment.	Standard		Best selected	Electro- lytic	Wire Bars
	Cash	3 Months			
£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
55 13 9	55 13 11	56 2 5	61 2 1	62 5 6	62 9 8

The following pages give examples of commercial "Account Sales" for Argentiferous Copper material (in this case, "Cement Copper"), and "*Pro Forma*" Invoices for the sale of Copper Matte and Blister Copper. The figures show the realizable value of the different parcels after the buyers' deductions for treatment and profit.

A . . . B . . . & CO., LTD.

SWANSEA.

ACCOUNT SALES.

Description_____ *Argt. Copper Material* _____

Date of sampling_____ *5th October, ...* _____

On Account of_____ *Messrs. C . . . D . . . & Co.* _____

Bags	Net weight.	Moisture.	Loss.	Dry weight.
5,200	154 11 0 0 =	154.55	19%	29.36
Tare	4 1 1 0			125.19

158 12 1 0

<i>Assays.</i>		<i>Contents.</i>	<i>£</i>	<i>s.</i>	<i>d.</i>
Silver	63.5 oz.	7,950 oz. @ 26 ½d per oz.	865	7	10
Copper	64.7% dry.	81.00 @ 62.25 per ton.	5,042	5	0
<i>Less penalties for Chlorine 1.18% }</i>			5,907	12	10
<i>" " " Bismuth 0.60% }</i>			125	4	0
			5,782	8	10
<i>Less weighing and sampling expenses .</i>			2	2	0
			<u>£5,780</u>	<u>6</u>	<u>10</u>

Due in cash, 8th December, 19—.

Prices.

Silver at Spot Standard d/Sampling 26 ½d p. oz.

Copper B.S. d/Sampling £62 5= 62.250 p. ton

Less 3½% 2.178

Returning Charge 10.000 £12.178 ..

£50.072 .. net

Delivery_____ *Our works* _____

A . . . B . . . & CO., LTD.

SWANSEA.

26th October, ...

PRO-FORMA INVOICE FOR ARGENTIFEROUS COPPER MATTE

Net Weight . . . 400 tons of 2,240 lb.

Moisture 0.5% . . . 2 „

398 „ dry weight

Copper 50% wet assay.

Less 1.3

48.7%	-	<i>Engineering & Mining Journal's</i> price for electro. wire bars of 14c. per lb., less 1½c. = 12½c. . . .	\$54,271.25
		Less 1%	542.71

\$53,728.54

Silver—50 oz. per long ton = 19.900 oz.

95% = 18,905 oz. @ N.Y. price of

56c. per oz.¹ 10,586.80

\$64,315.34

Delivery—*C.I.F. New York* ;

60c. per ton lighterage at shipper's expense.

PRO-FORMA INVOICE FOR BLISTER COPPER

Net Weight . . . 200 tons of 2,240 lb.

Copper—98% assay	@	<i>Engineering & Mining</i> <i>Journal's</i> price for electro. wire bars of 14c.	\$62,720.00
		Less 1%	627.20

\$62,092.80

Silver—100 oz. per long ton = 20,000 oz. @

56c.¹ 11,200.00

\$73,292.80

Returning Charge—\$15 per short ton—2,000 lb. 3,360.00

\$69,932.80

Delivery—*C.I.F. New York* ;

60c. per ton lighterage at shipper's expense.

¹ Fine silver price (999 fine).

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| Aluminium. (MORTIMER.) | Drugs in Commerce. (HUMPHREY.) |
| Anthracite. (SUMMERS.) | Dyes. (HALL.) |
| Asbestos. (SUMMERS.) | Electric Lamp Industry, The. (PERCIVAL.) |
| Bookbinding Craft and Industry. (HARRISON.) | Electricity. (NEALE.) |
| Books—From the MS. to the Book-seller. (YOUNG.) | Engraving. (LASCELLES.) |
| Boot and Shoe Industry, The. (HARDING.) | Explosives, Modern. (LEVY.) |
| Bread and Bread Baking. (STEWART.) | Fertilizers. (CAVE.) |
| Brushmaker, The. (KIDDIER.) | Film Industry, The. (BOUGHEY.) |
| Butter and Cheese. (TISDALE and JONES.) | Fishing Industry, The. (GIBBS.) |
| Button Industry, The. (JONES.) | Furniture. (BINSTEAD.) |
| Carpets. (BRINTON.) | Furs and the Fur Trade. (SACHS.) |
| Clays and Clay Products. (SEARLE.) | Gas and Gas Making. (WEBBER.) |
| Clocks and Watches. (OVERTON.) | Glass and Glass Making. (MARSON.) |
| Clothing Industry, The. (POOLE.) | Gloves and the Glove Trade. (ELLIS.) |
| Cloths and the Cloth Trade. (HUNTER.) | Gold. (WHITE.) |
| Coal. (WILSON.) | Gums and Resins. (PARRY.) |
| Coal Tar. (WARNES.) | Incandescent Lighting. (LEVY.) |
| Coffee—From Grower to Consumer. (KEABLE.) | Ink. (MITCHELL.) |
| Cold Storage and Ice Making. (SPRINGETT.) | Iron and Steel. (HOOD.) |
| Concrete and Reinforced Concrete. (TWELVETREES.) | Ironfounding. (WHITELEY.) |
| Copper—From the Ore to the Metal. (PICARD.) | Jute Industry The. (WOODHOUSE and KILGOUR.) |
| Cordage and Cordage Hemp and Fibres. (WOODHOUSE and KILGOUR.) | Knitted Fabrics. (CHAMBERLAIN and QUILTER.) |
| Corn Trade, The British. (BARKER.) | Lead, including Lead Pigments. (SMYTHE.) |
| Cotton. (PEAKE.) | Leather. (ADCOCK.) |
| | Linen. (MOORE.) |
| | Locks and Lock Making. (BUTTER.) |
| | Match Industry, The. (DIXON.) |
| | Meat Industry, The. (WOOD.) |

Common Commodities and Industries—contd.

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| Motor Industry, The. (WYATT.) | Stones and Quarries. (HOWE.) |
| Nickel. (WHITE.) | Straw Hats. (INWARDS) |
| Oil Power. (NORTH.) | Sugar. (MARTINEAU.) (Revised by EASTICK) |
| Oils. (MITCHELL.) | Sulphur and Allied Products. (AUDEN.) |
| Paints and Varnishes. (JENNINGS.) | Talking Machines. (MITCHELL.) |
| Paper. (MADDOX.) | Tea. (IBBFTSON.) |
| Patent, Smokeless, and Semi-Smokeless Fuels. (GREENE and PERKIN.) | Telegraphy, Telephony, and Wireless. (POOLE.) |
| Perfumery, The Raw Materials of. (PARRY.) | Textile Bleaching. (STEVEN.) |
| Photography. (GAMBLE.) | Timber. (BULLOCK.) |
| Platinum Metals, The. (SMITH.) | Tin and the Tin Industry. (MUNDEY.) |
| Player Piano, The. (WILSON.) | Tobacco. (TANNER.) (Revised by DREW.) |
| Pottery. (NOKE and PLANT.) | Velvet and the Corduroy Industry. (COOKE.) |
| Rice. (DOUGLAS.) | Wall Paper. (WARD.) |
| Rubber. (STEVENS and STEVENS.) | Weaving. (CRANKSHAW.) |
| Salt. (CALVERT.) | Wheat and Its Products. (MILLAR.) |
| Shipbuilding and the Shipbuilding Industry. (MITCHELL.) | Wine and the Wine Trade. (SIMON.) |
| Silk. (HOOPER.) | Wool. (HUNTER.) |
| Silver. (WHITE.) | Worsted Industry, The. (DUMVILLE and KERSHAW.) |
| Soap. (SIMMONS.) | Zinc and Its Alloys. (LONES.) |
| Sponges. (CRESSWELL.) | |
| Starch and Starch Products. (AUDEN.) | |

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